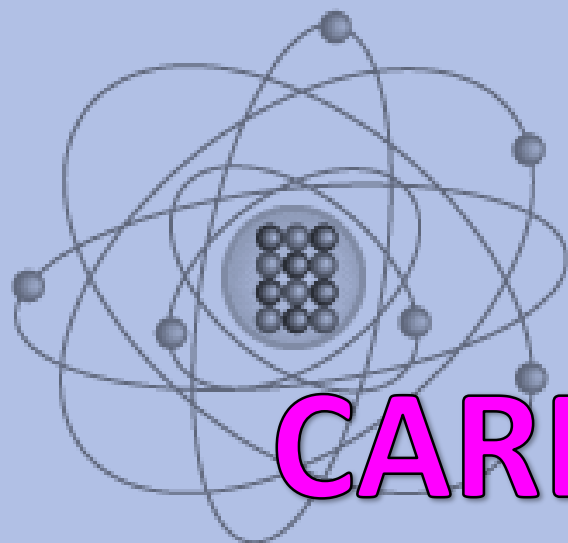


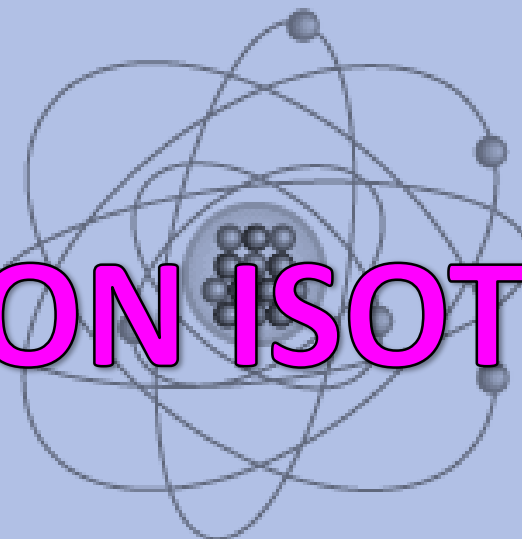
For the students of Paleoclimatology, Climatology, and Climate Models (ECD II year - 1st semester 2024/25), please note that the only topics that will be covered in the exam are the following:

- The carbon cycle
- The carbon reservoirs
- The carbon fluxes and exchanges among reservoirs
- The silicate weathering

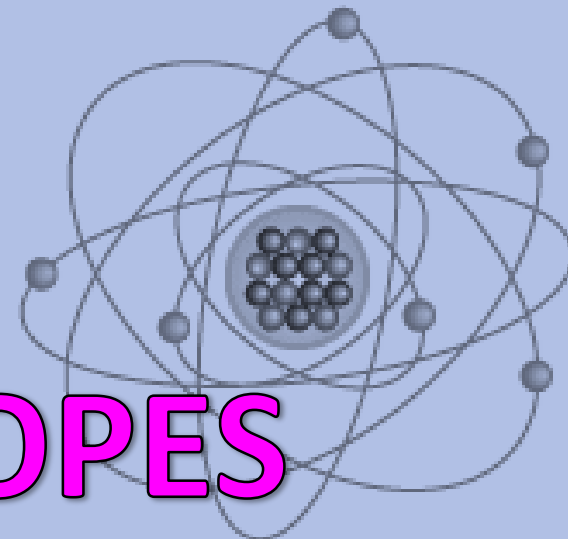
CARBON ISOTOPES



Carbon-12
stable



Carbon-13
stable



Carbon-14
unstable (radioactive)

 Proton

 Neutron

 Electron

SUMMARY

- Why Carbon Isotopes Matter
- Reviewing the Carbon Cycle
- Carbon Cycling in Oceans
- Examining $\delta^{13}\text{C}$ variations across different time scales (Suborbital, Orbital, Geological-Tectonic): Short and Long-Term Changes
- Exploring Local Factors Affecting Productivity, Ocean Circulation, and Carbon Cycling
- Practical Applications
- Impacts on Mass Extinctions
- Insights into Sapropel Formation

WASTE DATA?

Carbon isotope data have been consistently gathered since the 1950s, coinciding with the stable oxygen isotope revolution. As CO_2 is employed for $\delta^{18}\text{O}$ measurements, and the spectrometer allows concurrent measurement of two isotopes, carbon isotope data has been simultaneously collected. CO_2 with ^{12}C and ^{13}C has molecular masses ranging from 44 to 46, enabling the determination of $\delta^{13}\text{C}$ using the spectrometer.

Initially, $\delta^{13}\text{C}$ data was collected without any specific purpose. Despite temperature having little impact on isotope fractionation, the intriguing signal, not displaying a flat trend, prompted the utilization of data obtained from the analysis of CaCO_3 found in fossils like foraminifera.

For a while, $\delta^{13}\text{C}$ data remained underutilized, despite revealing intriguing trends often correlated with $\delta^{18}\text{O}$. The process of photosynthesis contributed to C isotope fractionation, potentially influencing the observed values.

$\delta^{13}\text{C}$: WHERE AND WHY?

Stable carbon isotopes data can be extracted from analyses of planktonic and benthic foraminifera, the total carbon content in rocks or carbonate nodules within paleosols, bone material (collagen), and organic matter within sediment. These data hold significant relevance in the fields of Paleoclimatology, Paleoecology, Geology, and Paleontology, despite their intricate interpretation due to their involvement in complex, interconnected biogeochemical cycles.

Their significance lies in their capacity to offer insights into the past carbon cycle, which played an important role in shaping past and present climate conditions.

Carbon isotopes serve as valuable tools for:

1. providing essential paleoecological, paleoenvironmental, and paleoceanographic information,
2. allowing precise stratigraphic correlation.

$\delta^{13}\text{C}$, CO_2 AND CLIMATE

The connection between $\delta^{13}\text{C}$ and photosynthesis gained prominence in the 1970s, coinciding with the emergence of the "global warming" debate linked to anthropogenic CO_2 emissions into the atmosphere. A fundamental question arose: does CO_2 influence the climate?

The focus on $\delta^{13}\text{C}$ data arose from this observation: **the intensity of photosynthesis in surface ocean waters regulates the partial pressure of CO_2 in the atmosphere above.** Therefore, it was reasonable to consider that $\delta^{13}\text{C}$ variations could serve as a "proxy" for past atmospheric CO_2 partial pressure. Although not without complexities, this possibility ignited a surge in research and, as with oxygen, led to significant advancements.

Let's proceed step by step...

We start unraveling certain aspects/mechanisms of the carbon cycle.

BASICS OF THE CARBON CYCLE

A substantial quantity of carbon (C) exists in the Universe and on Earth. On our planet, it serves as a “VITAL” element, playing a crucial role in numerous biological and geological processes.

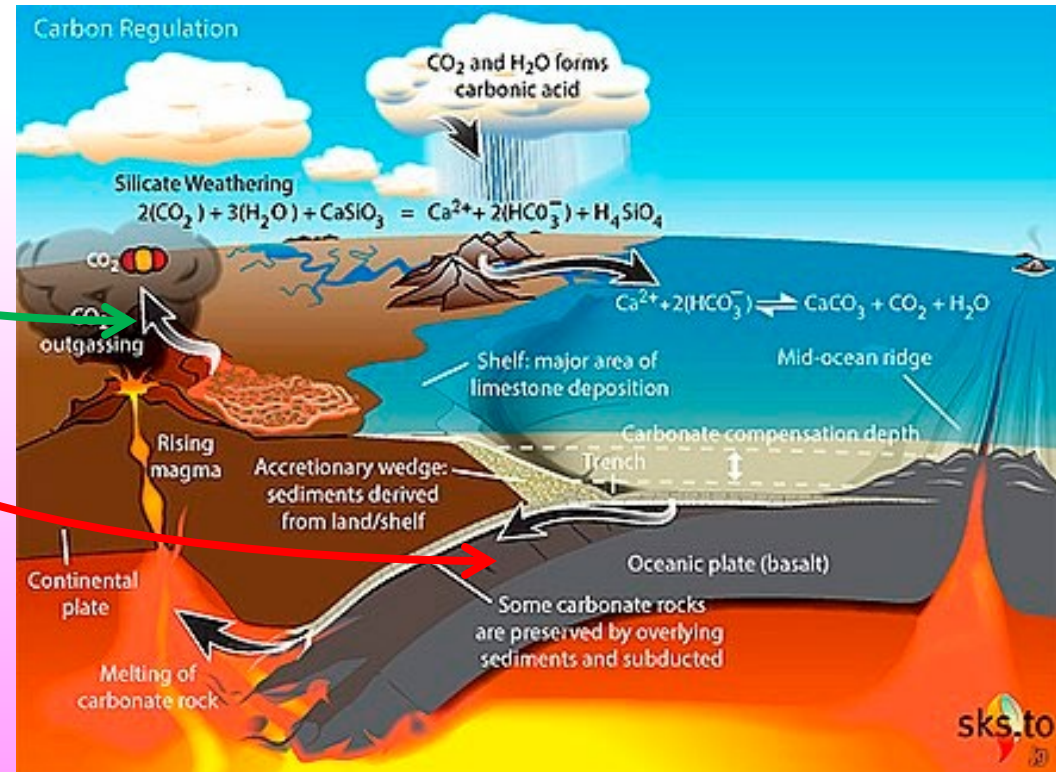


BIO-GEO-CHEMICAL CARBON CYCLE

...but also...

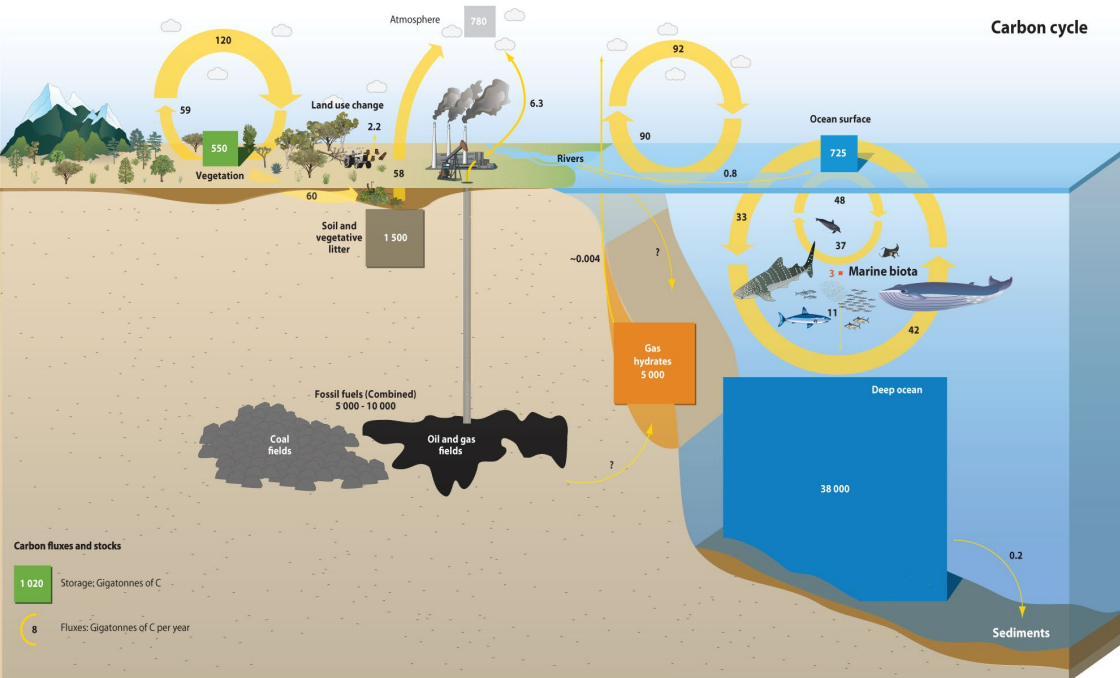
mantle-crust exchanges (slow): e.g., **volcanism** (C volcanic outgassing) and **subduction** (C storage).

We will focus mainly on the so-called **EXOGENIC SYSTEM** (Hydrosphere/Cryosphere, Atmosphere, Lithosphere, Biosphere)



CARBON RESERVOIRS

On Earth, carbon (C) is distributed across diverse reservoirs in varying quantities and forms. Carbon undergoes continuous exchange among these reservoirs.



- 1) ATMOSPHERE: 780 Gt
- 2) BIOSPHERE (terrestrial): 550 Gt
- 3) SOILS: 1500 Gt

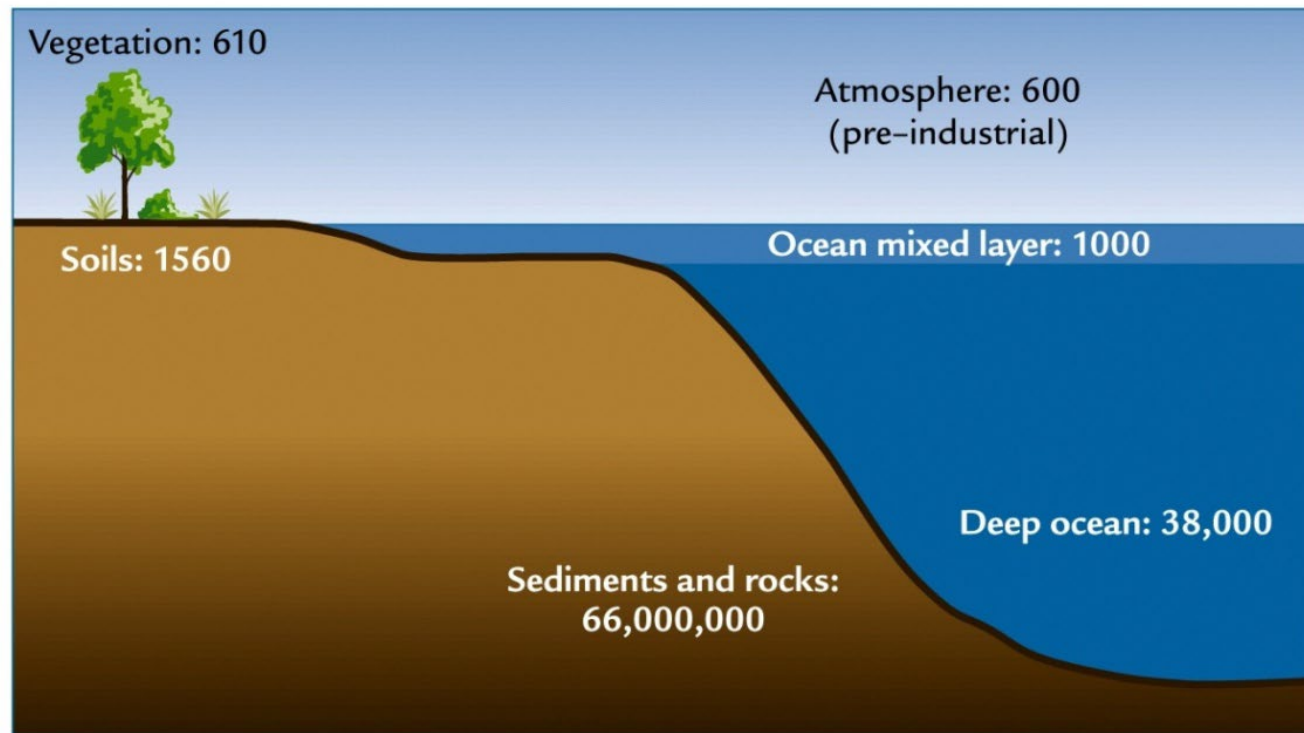
- 4a) "UPPER OCEAN": 725 Gt
- 4b) "DEEP OCEAN": 38.000 Gt

- 5) ROCKS E SEDIMENTS: $66 \cdot 10^6$ Gt
- 6) COALS E ROCKS: $20 \cdot 10^6$ Gt

In the atmosphere, the majority of carbon exists as CO_2 , while in **soils and the biosphere**, it is present as organic matter (C_{org}).

Geological reservoirs, such as rocks, sediments, coal, store carbon in the form of CaCO_3 (inorganic) or as dispersed organic matter (C_{org}), oil, and coal.

ATMOSPHERE / OCEAN RELATIONSHIP



A

Major carbon reservoirs (gigatons)

The deep ocean reservoir, comprising 38,000 Gt C, vastly surpasses the size of both the atmosphere (600 Gt C) and the upper ocean (1000 Gt C). Over 90% of the carbon within the ocean-atmosphere system resides in the deep ocean, emphasizing that "the atmosphere is the slave of the ocean."

ANOTHER GEOLOGICAL RESERVOIR: CLATHRATE HYDRATES /GAS HYDRATES

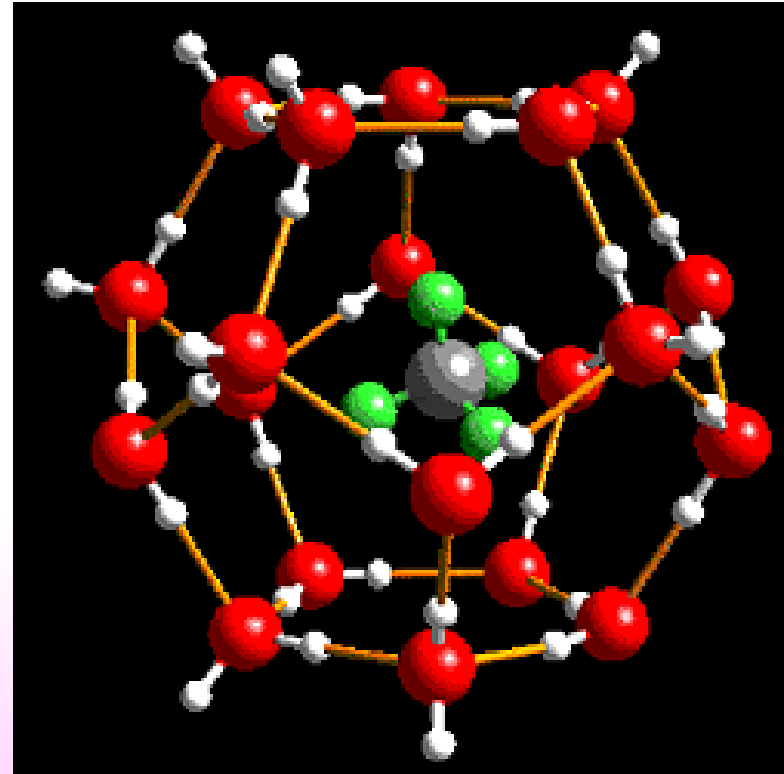
Until recently, the carbon cycle was predominantly defined by two "geological" reservoirs:

Carbon stored in CaCO_3

Carbon stored in organic matter.

However, in recent times, a new reservoir has been introduced:

CLATHRATES are **crystalline compounds** that develop when water interacts with small gaseous molecules, typically at **near-zero temperatures and high pressures** (a few tens of atmospheres) – conditions commonly found on the seafloor. They can swiftly transition from a solid to a gaseous state when exposed to ambient pressure and temperature, liberating methane gas and water. Of particular significance are clathrates composed of hydrocarbons such as methane (CH_4), ethane (C_2H_6), propane (C_3H_8), and carbon dioxide (CO_2).



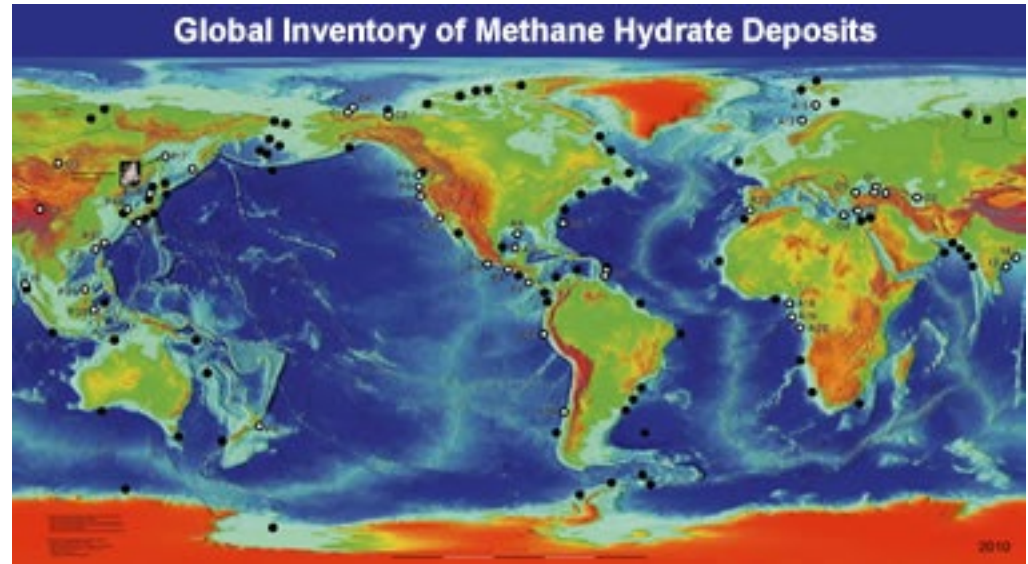
Structure of a clathrate gas

The most common host molecule in natural gas hydrates is methane, CH_4 . In this figure, methane is represented by a gray atom (carbon) surrounded by four hydrogen atoms (green), trapped in a cage of water molecules (red oxygen, white hydrogen).

CLATHRATE HYDRATES : *ICE THAT BURNS*



GAS HYDRATES. Subduction zone (Oregon, USA)



Global inventory of methane hydrates deposits

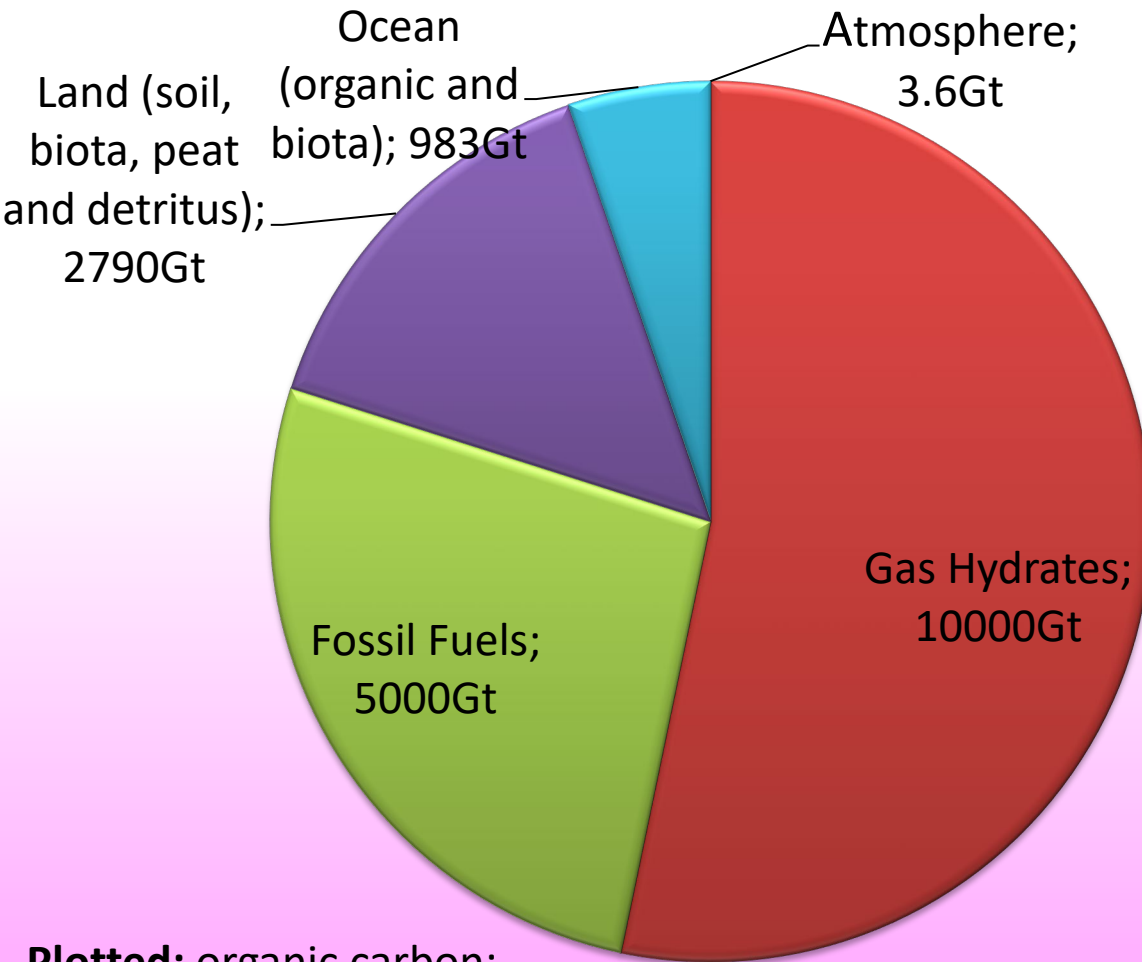


Clathrates become unstable at atmospheric pressure.

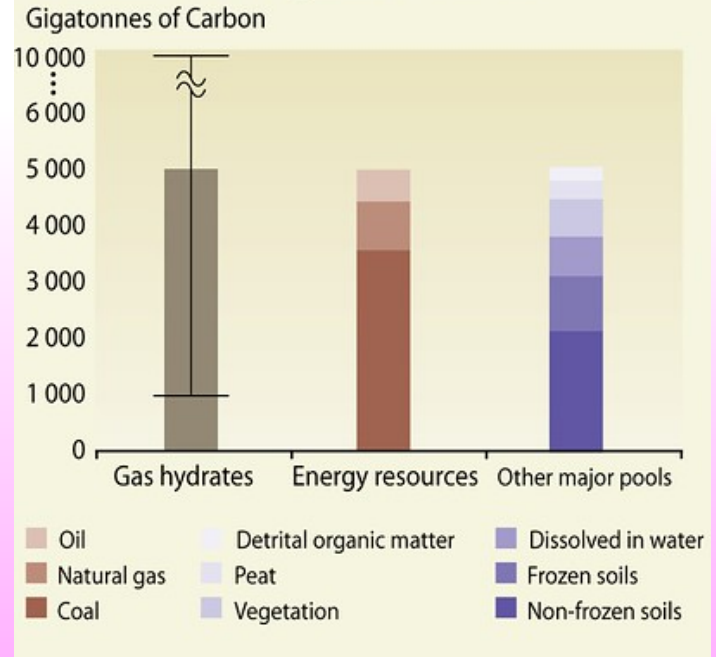
When ignited, the hydrocarbons within the clathrate structure combust and convert ice (solid H_2O) into liquid water (H_2O)

HOW MUCH CARBON IN THE CLATHRATES?

Size of organic carbon reservoirs (Kvenvolden, 1998)



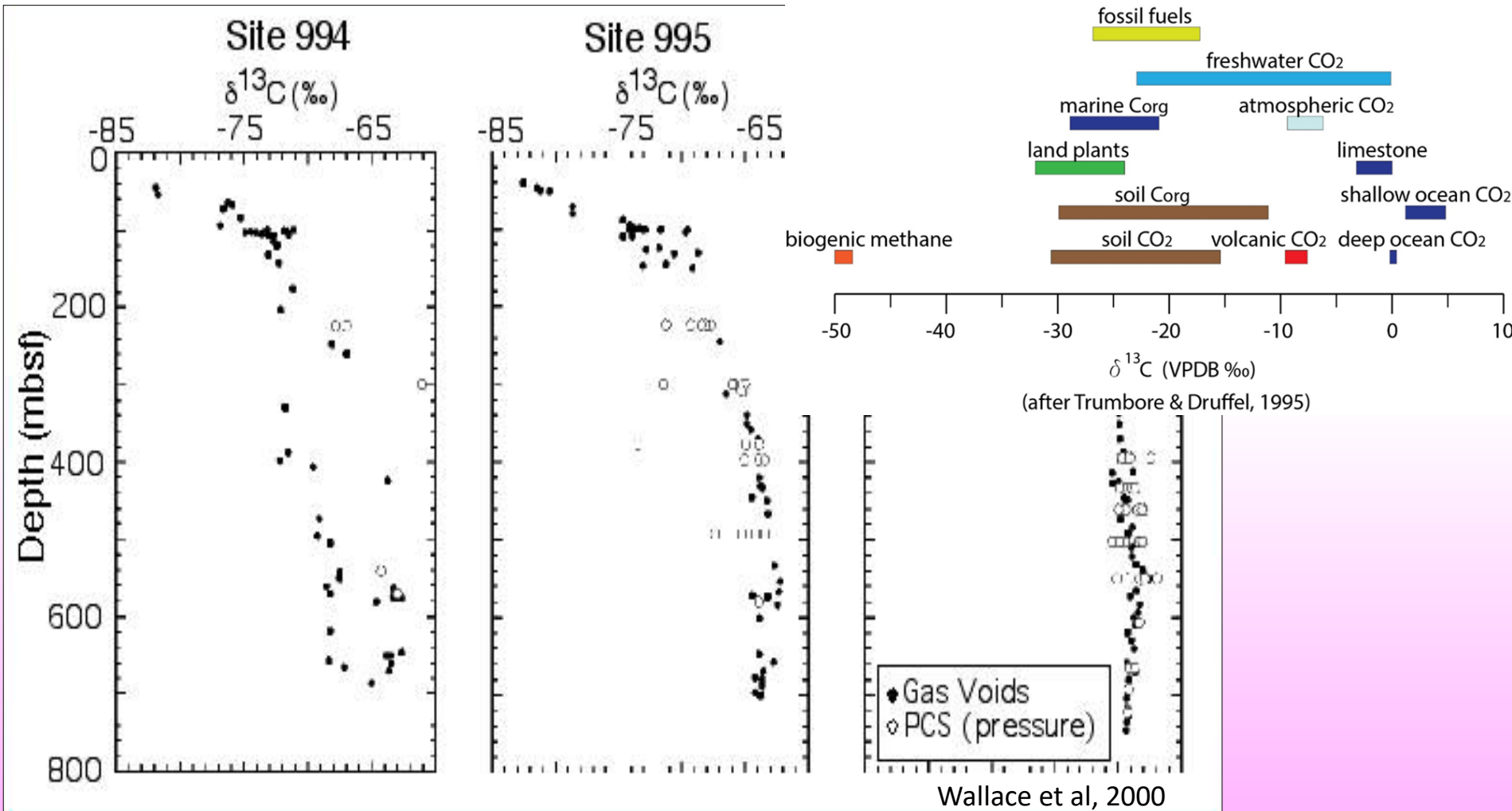
Carbon mass in gas-hydrate-bound methane compared to other sources of organic carbon



Plotted: organic carbon:

Not plotted: dispersed organic carbon (kerogen, bitumen). This would be three orders of magnitude larger.

$C_{Clathrate}$ ISOTOPIC COMPOSITION



Methane $\delta^{13}C$ profiles (Blake Ridge, Florida). Note the negative values of $\delta^{13}C$ (< -60 ‰).

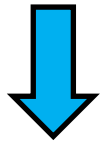
CLATHRATES DISSOCIATION: GEOHAZARD

Clathrates are stable at **High P** and **low T** conditions

Their dissociation occurs in conditions of instability:

when the pressure drops (sea level drops)

when the temperature rises



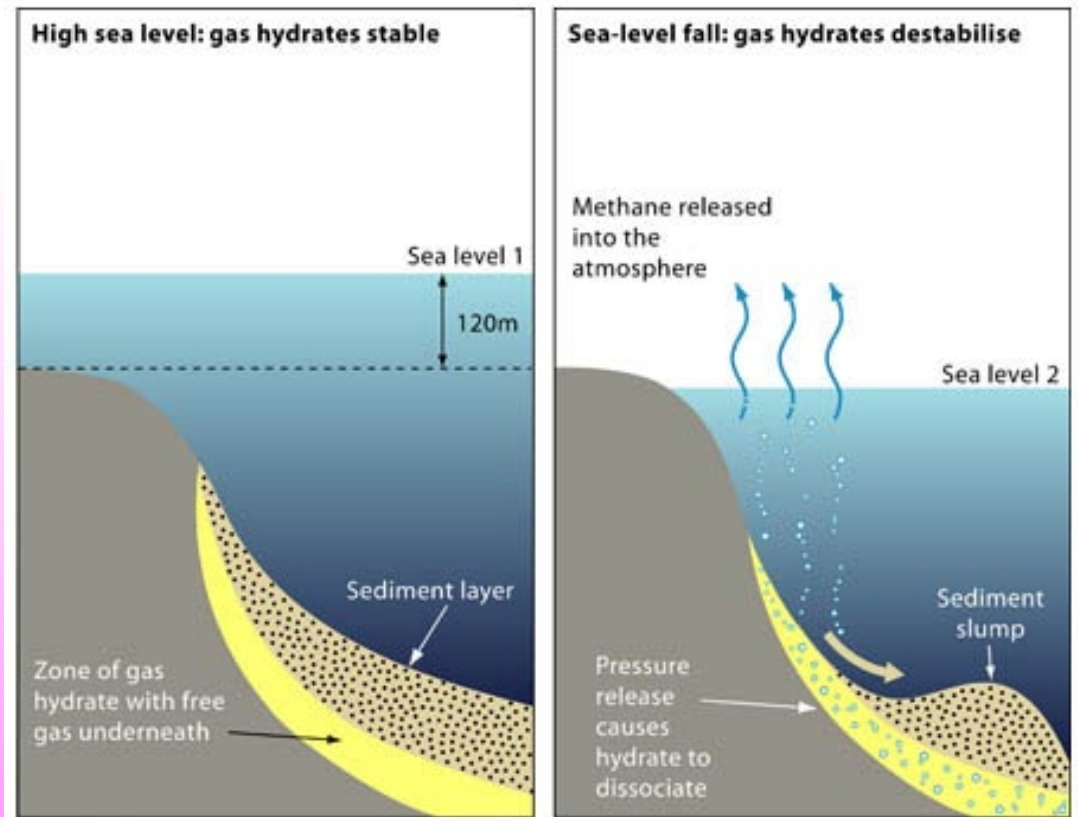
CLIMATIC RISK



An increase in ocean temperatures leads to the dissociation of gas hydrates, triggering the release of significant CO_2 . This, in turn, contributes to further warming and additional gas hydrate dissociation, establishing a positive feedback loop.



ENVIRONMENTAL RISK



CARBON IN THE OCEANS

4a) "UPPER OCEAN": 1000 Gt

4b) "DEEP OCEAN": 38.000 Gt

Carbon in the oceans exists in various chemical forms:

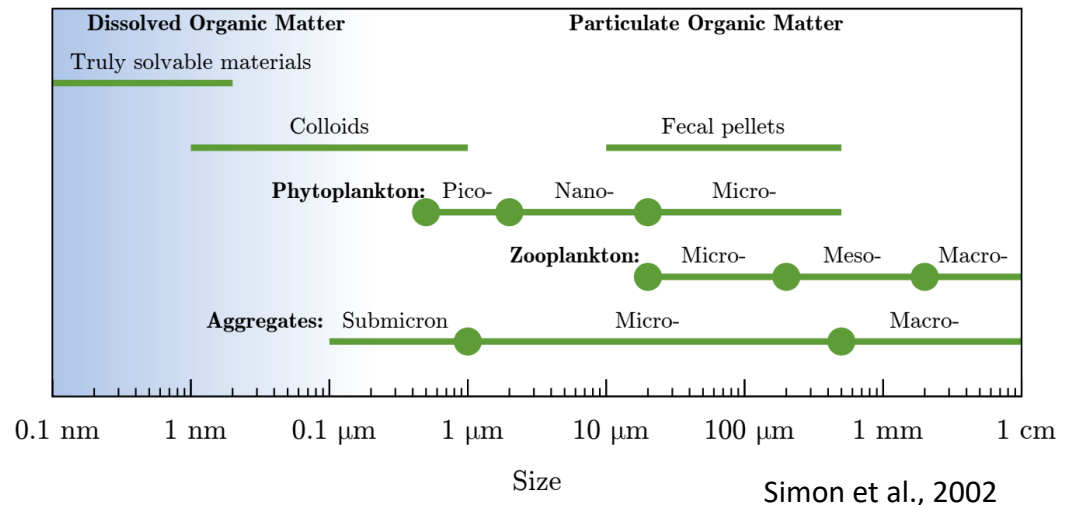
A small portion (around 13-23 Gt C) is in form of living organisms and discrete organic compounds in suspension (**POC = Particulate Organic Carbon** - >1 μ m).

A portion (approximately 685 Gt C) exists as dissolved organic matter (**DOC = Dissolved Organic Carbon** -> <1 μ m).

The majority (about 38,000 Gt C) of oceanic carbon is in the form of inorganic compounds, referred to as **DIC (Dissolved Inorganic Carbon)**.

Ratio:

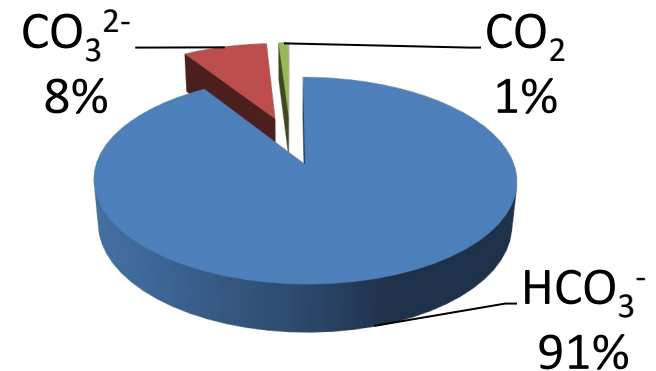
DIC : DOC : POC = 2000 : 38 : 1



DIC IN THE OCEAN

DIC (*Dissolved Inorganic Carbon*) or **TDIC** (*Total Dissolved Inorganic Carbon*) in the ocean ("upper ocean" e "deep ocean") are in form of:

- 1) Carbon dioxide: CO_2 (1%)
- 2) Bicarbonate ion : HCO_3^- (91%)
- 3) Carbonate ion : CO_3^{2-} (8%)
- 4) Carbonic Acid: H_2CO_3 (trace)



The relationships between the three components of the DIC are governed by the following equation of equilibrium:



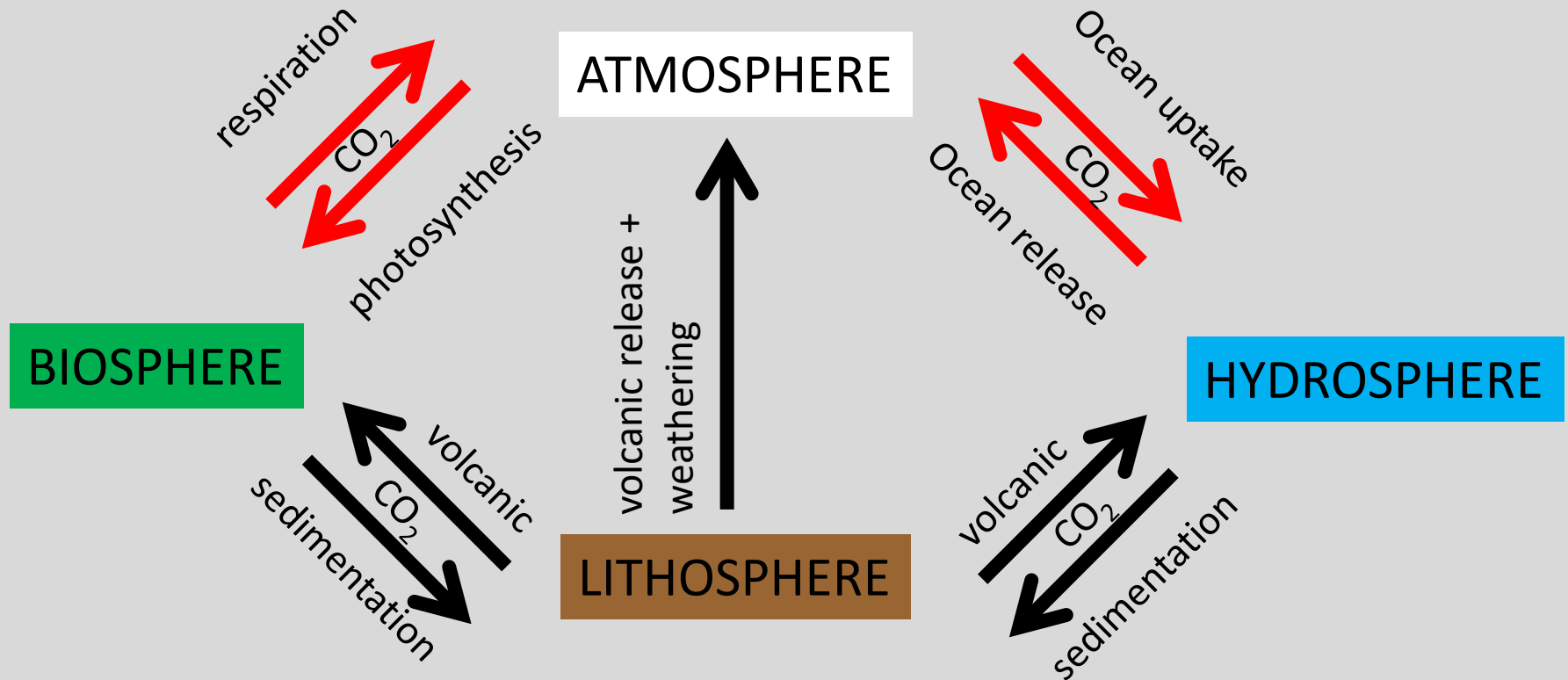
The ratios between these compounds determine the pH of the water - $[\text{H}^+]$. Only CO_2 can be exchanged with the atmosphere. The absorption of CO_2 increases the $p\text{CO}_2$ in the water and at the same time there is a shift in favor of HCO_3^- and against CO_3^{2-} .

→ The increase in the concentration of CO_2 in the water causes "acidification" and possible dissolution of the carbonate.

CARBON EXCHANGES AMONG RESERVOIRS

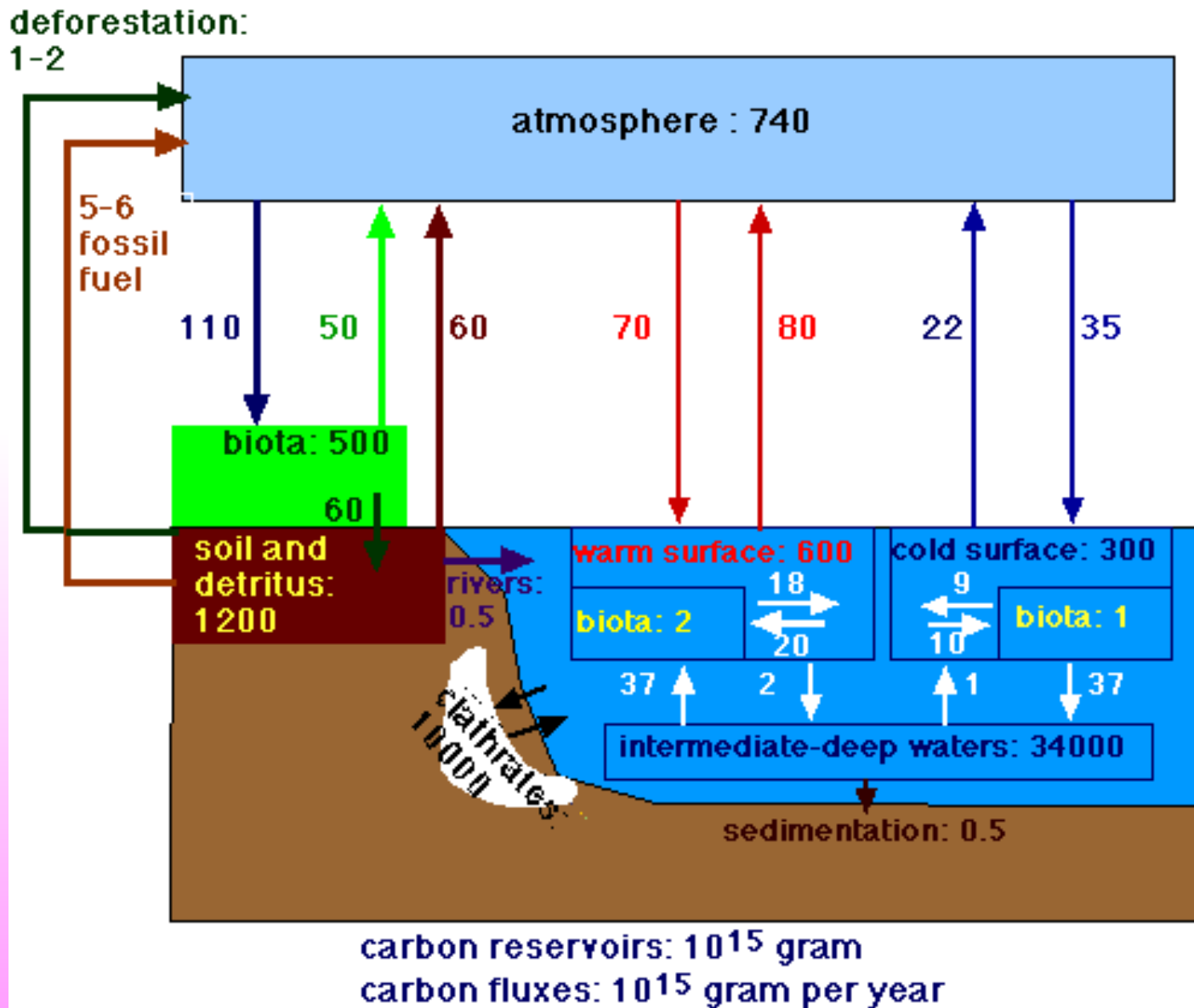
Carbon moves among the various "reservoirs" of the Earth, easily passing from the inorganic to the organic form.

→ shorth-term
→ Long-term

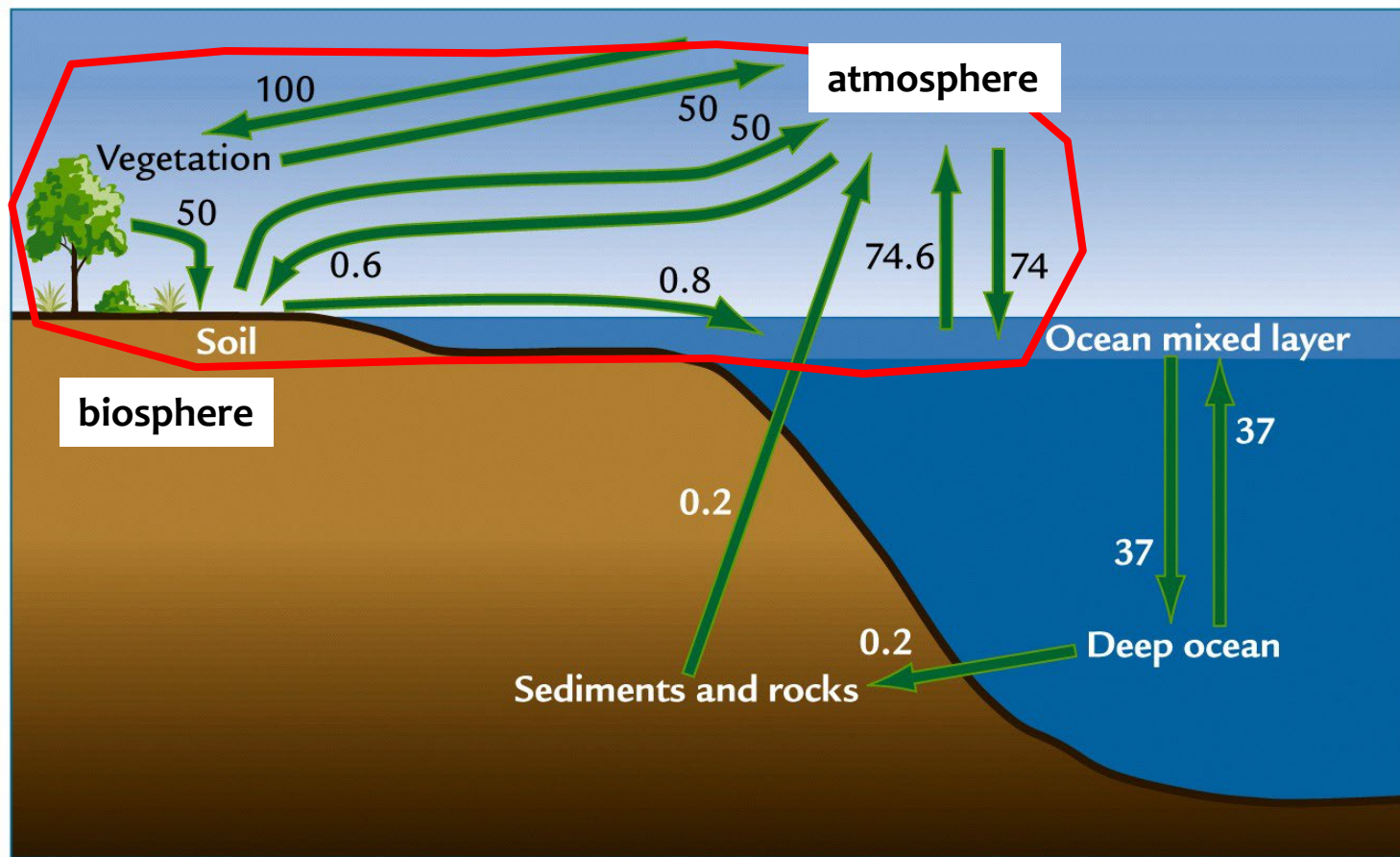


Exchanges take place mainly by means of CO₂ fluxes: hence the enormous importance of the carbon cycle for the global climate system. These fluxes insist on very different times.

CARBON FLUXES



RAPID FLUXES OF CARBON

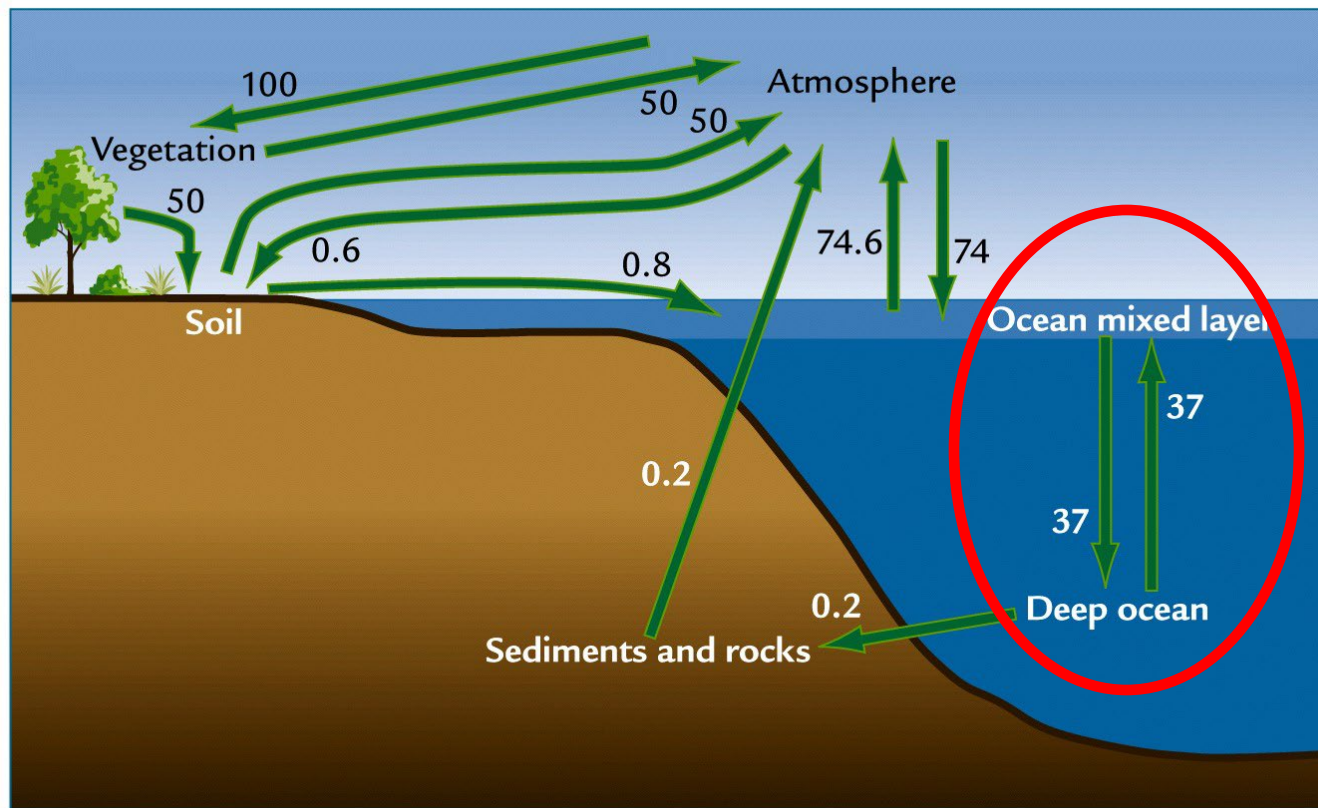


B

Carbon exchange rates (gigatons/year)

Exchanges of C are very rapid (years or a few tens of years) between the atmosphere and the biosphere (photosynthesis and respiration) and between the upper ocean and the atmosphere (among the smallest reservoirs).

SLOW FLUXES OF CARBON

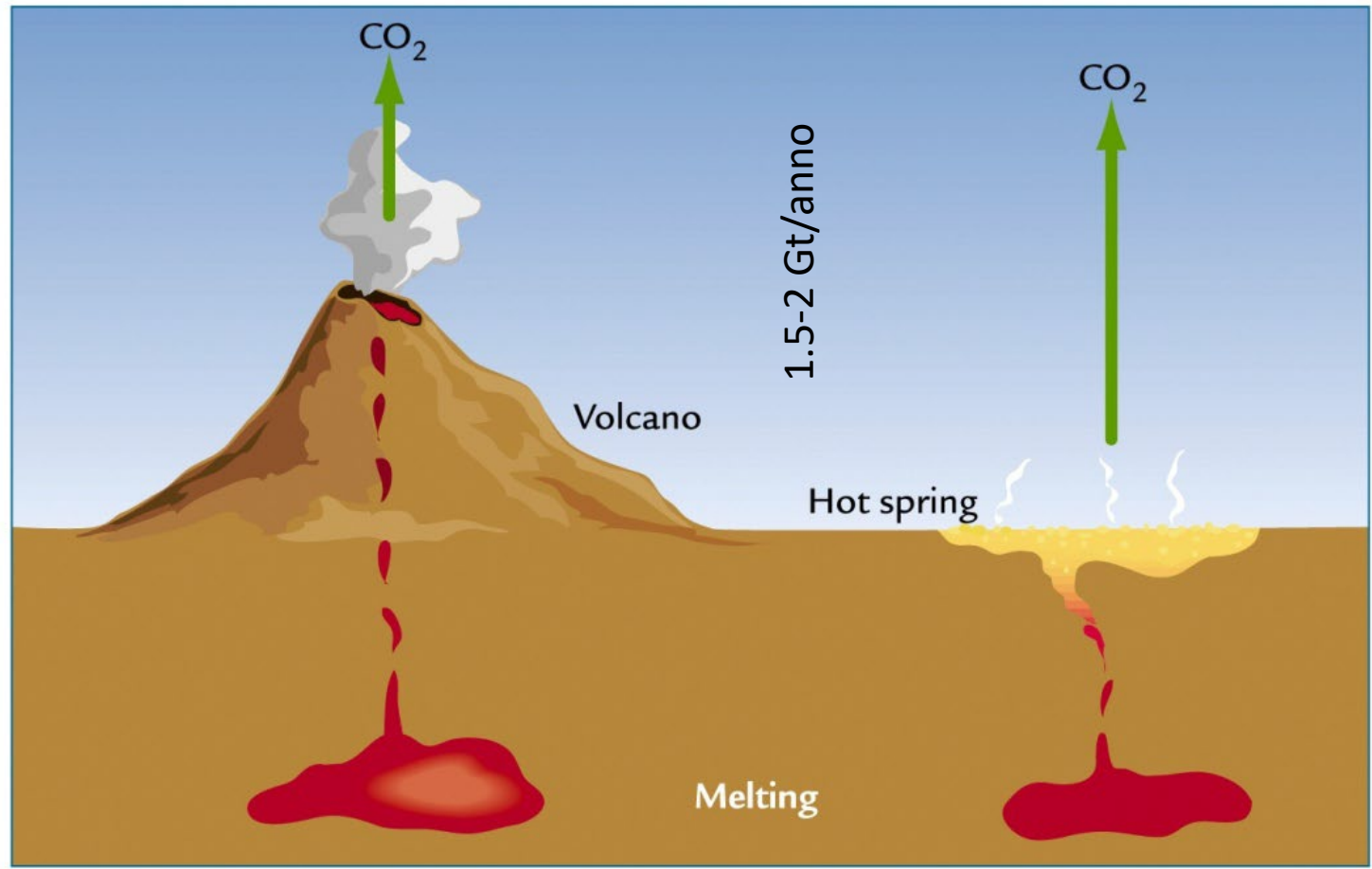


B

Carbon exchange rates (gigatons/year)

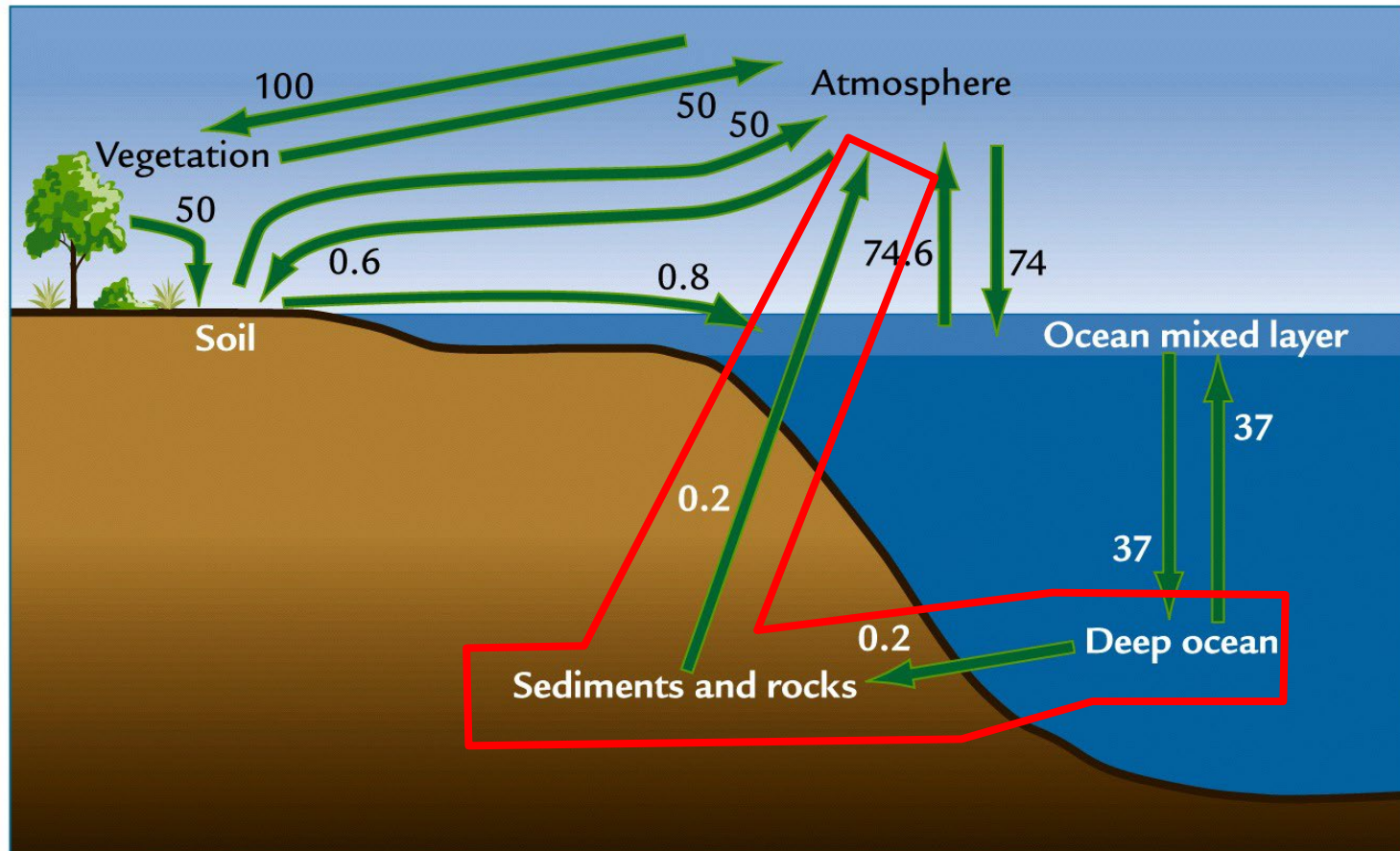
Exchanges of C between the upper and deep oceans are much slower; the two are separated from each other (e.g., thermocline) and exchanges are controlled by the general circulation (hundreds of years, up to 1500 years - oceanic mixing processes).

VERY SLOW FLUXES OF CARBON



Volcanoes and hydrothermal springs emit CO₂. This input is very variable over time: currently it is approx. 1.5-2.0 Gt C / year. The interior of the Earth is the ultimate source of C on the Earth's surface and has been continuous over geological time. Otherwise, the atmosphere would be free of CO₂.

VERY VERY SLOW FLUXES OF CARBON

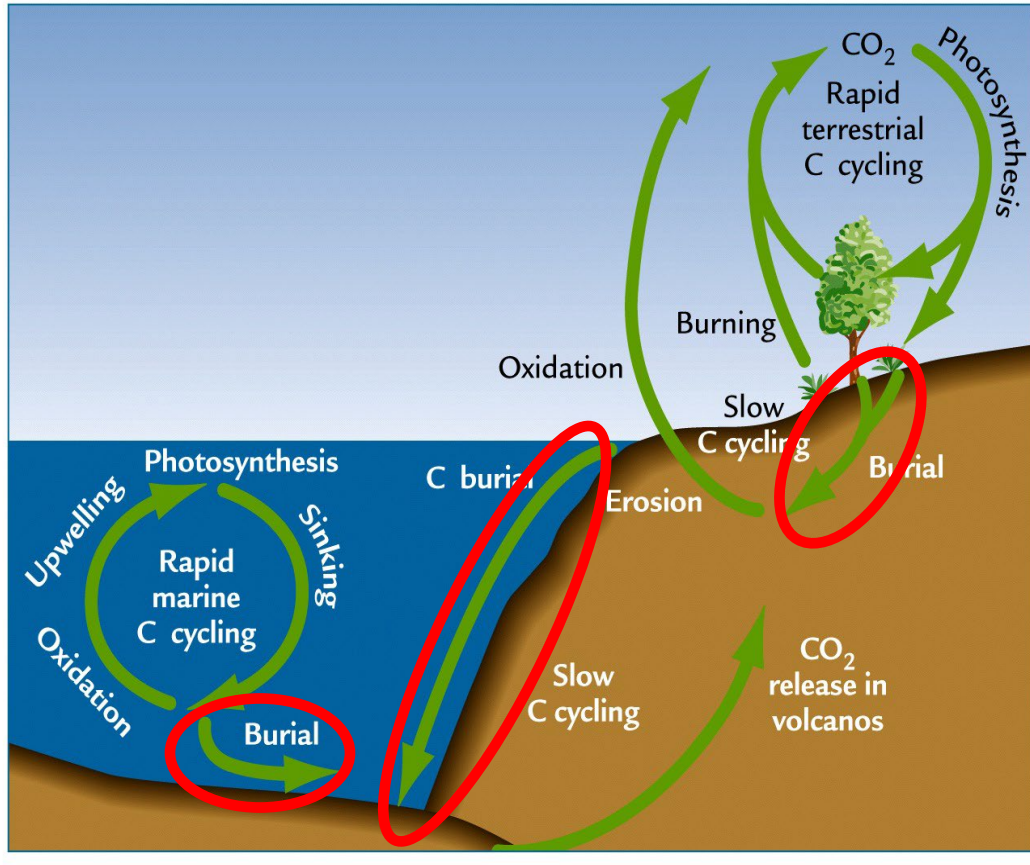


B

Carbon exchange rates (gigatons/year)

Exchanges of C between rocks / sediments and other reservoirs are very slow (from thousands to millions of years). Think of oil and sapropels, or black shales: they have been stores C for millions of years and will only return to circulation when they are exhumed and oxidized/wheated.

C_{org} IN THE GEOLOGICAL CYCLE



About 20% of C present on the Earth is in the form of C_{org} .

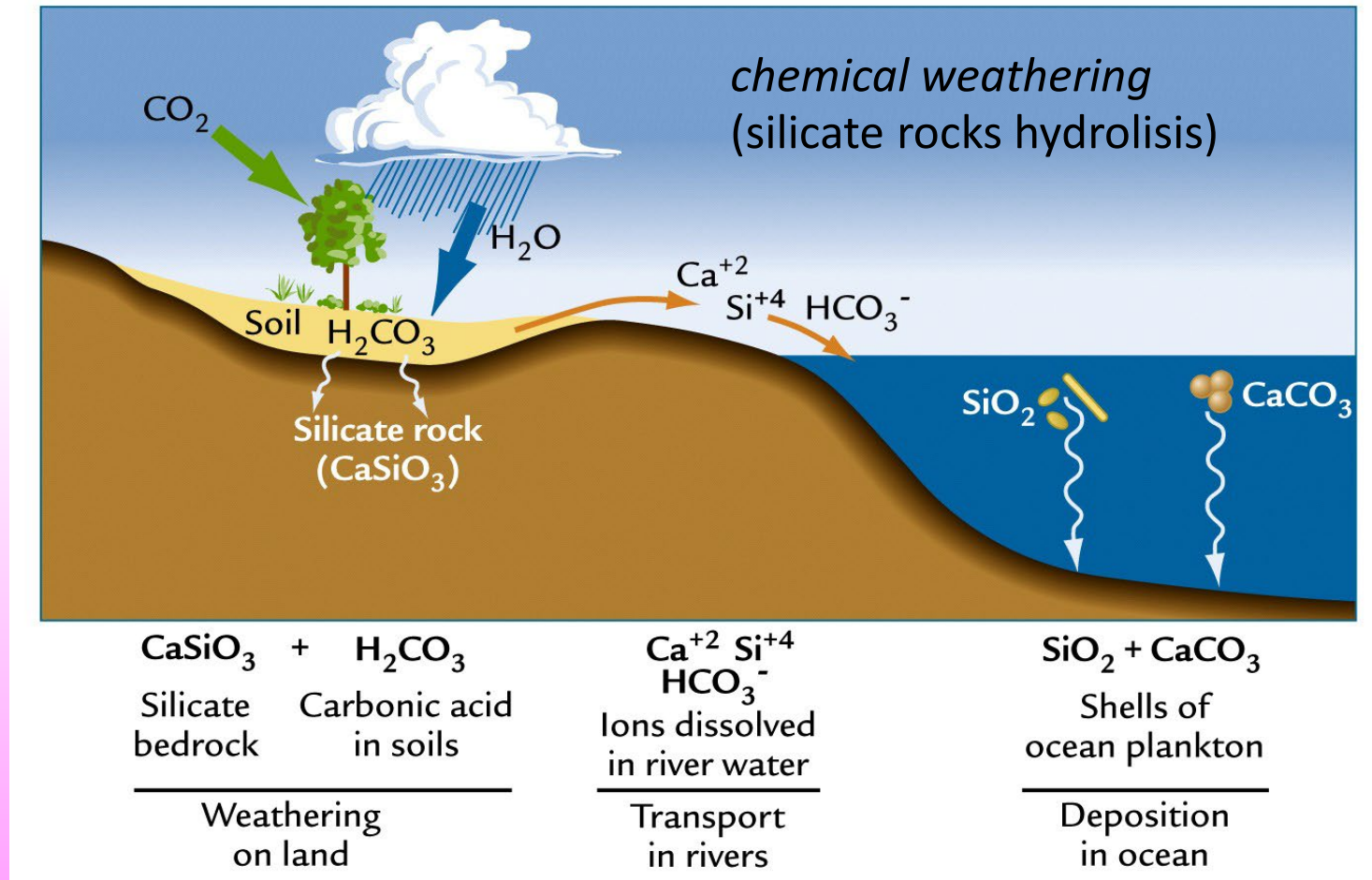
Most of it is quickly put back into circulation, but a small part is buried (marine sediments or continental deposits) and enters into the lithosphere.

Here it remains segregated for millions of years before being recycled in the ocean-atmosphere system.

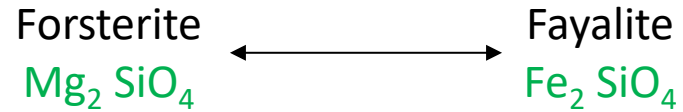
Generally, this is a slow process, but it is not always the case.

CARBON AND CHEMICAL WEATHERING

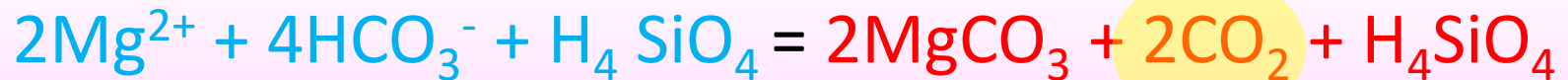
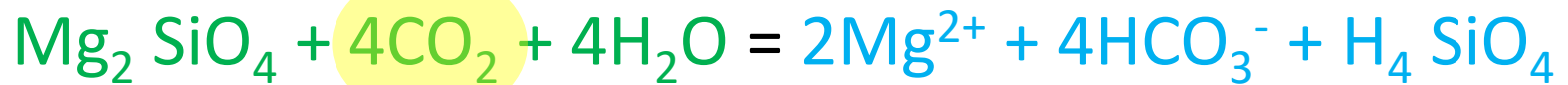
To avoid the excessive increase of CO_2 , a very effective mechanism is active: **the chemical alteration of the rocks on the earth's surface**; it occurs through two processes: **hydrolysis** and **dissolution**.



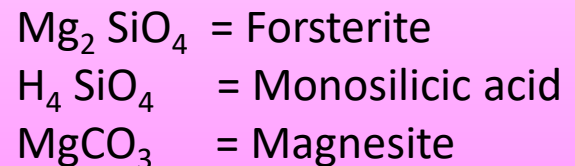
SILICATE ROCKS HYDROLISIS -1



1) Nesosilicates non-Al: Mg-Olivine (*Forsterite*)



Following the precipitation of magnesite, out of the 4 moles of CO_2 initially absorbed, only 2 are released back into the atmosphere as a gas..



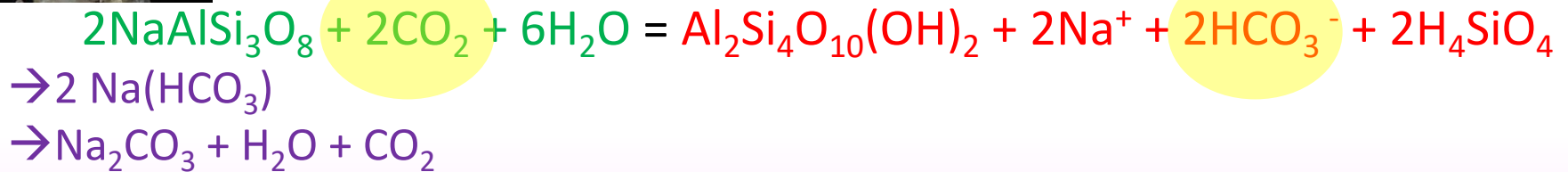
SILICATE ROCKS HYDROLISIS - 2

Feldspars → $\text{NaAlSi}_3\text{O}_8$ = Albite
 $\text{CaAl}_2\text{Si}_2\text{O}_8$ = Anorthite

$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ = Caolinite
 $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ = Montmorillonite
 H_4SiO_4 Silicic acid



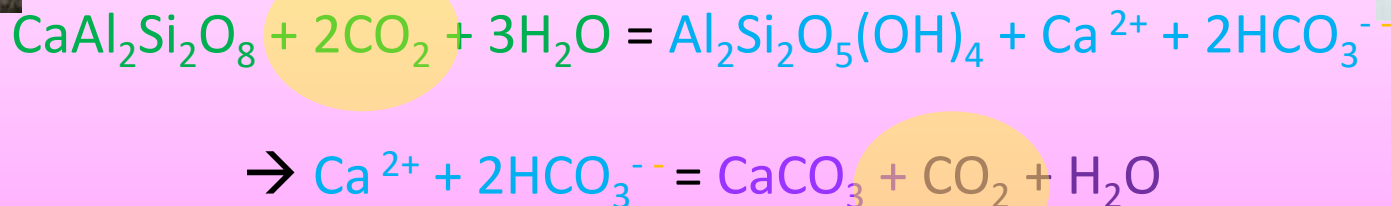
2) Aluminosilicates: Albite → Montmorillonite



Note: Sodium bicarbonate Nahcolite [$\text{Na}(\text{HCO}_3)$] or Natrite / Trona ($(\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O})$) only precipitates in extreme conditions (e.g., desert environment).



3) Aluminosilicates : es. Anorthite → Caolinite



As a consequence, after calcite precipitation, only 50% of the CO_2 is released back into the atmosphere as a gas.

DISSOLUTION (carbonate rocks):

MgCO₃ = Magnesite

CaCO₃ = Calcite



It's a completely reversible reaction, so there are no CO₂ "losses." Each mole of CO₂ consumed produces one mole of bicarbonate, which, when precipitated as carbonate, yields one mole of gaseous CO₂, resulting in a balanced equation.

This is a common occurrence in scenarios like karst formations (precipitation) and shell development (secretion).

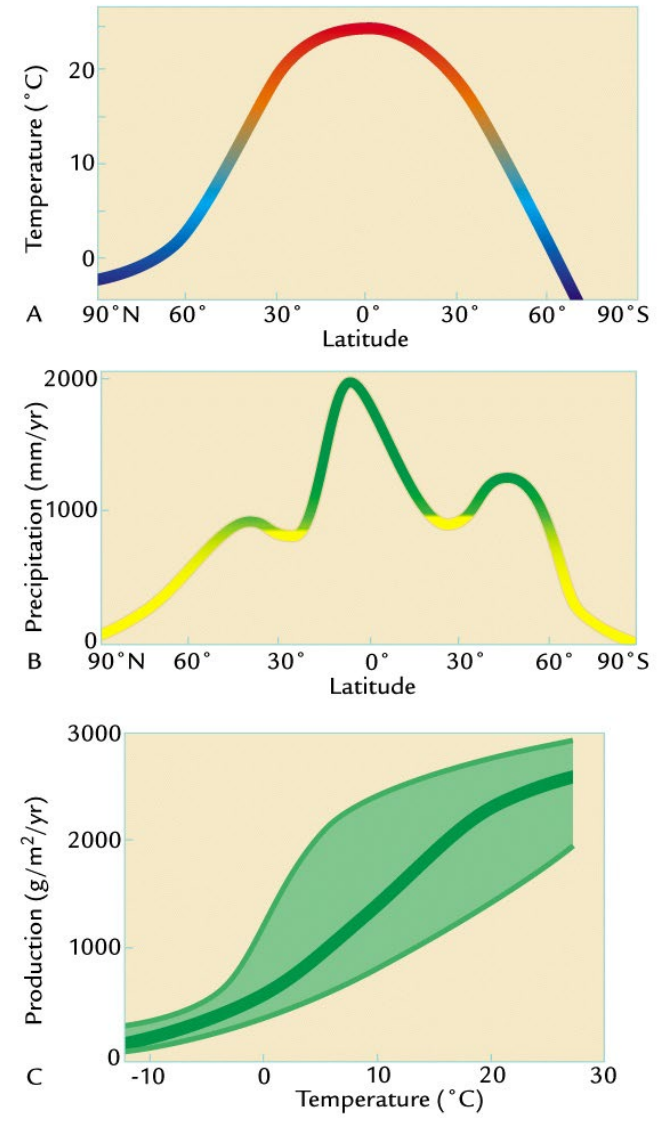
FACTORS CONTROLLING CHEMICAL WEATHERING

The rate of chemical weathering is influenced by three key factors:

TEMPERATURE: Higher temperatures result in increased weathering. Weathering is most active in regions with elevated temperatures.

RAINFALL: Greater precipitation leads to higher soil moisture levels. Water combines with CO_2 to form H_2CO_3 , intensifying weathering. Weathering is particularly strong in areas with high rainfall.

VEGETATION: Lush vegetation promotes increased weathering. Plants absorb CO_2 from the atmosphere and transport it to the soil, where it combines with water. Weathering is most effective in regions with abundant vegetation, often found in lower latitude

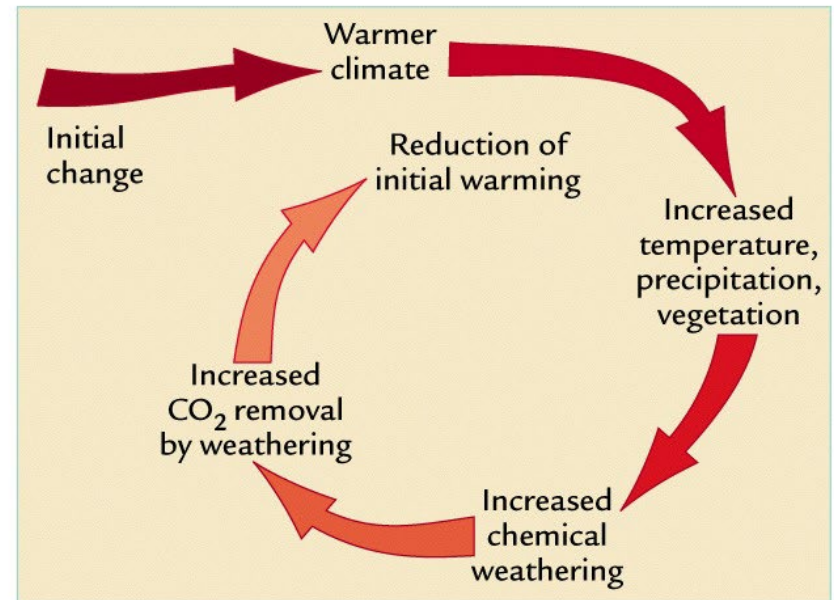


THE SILICATE PUMP

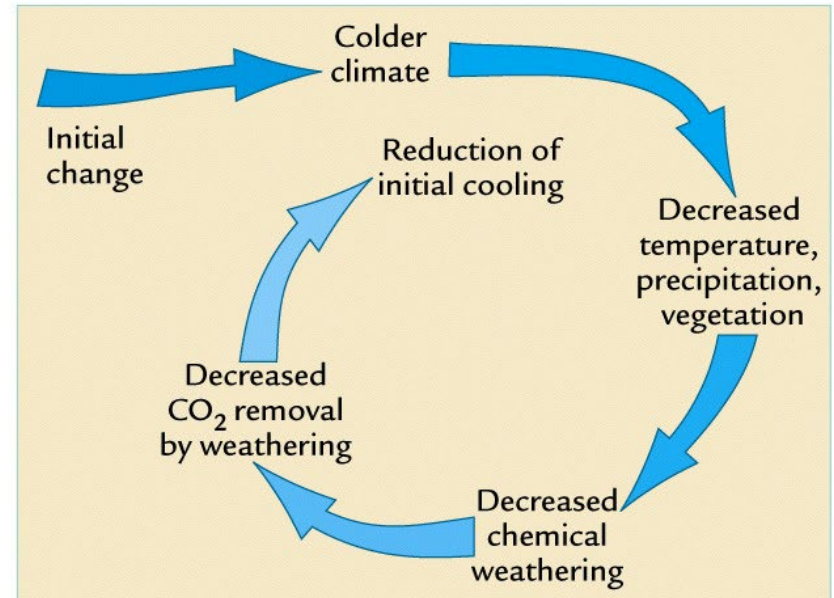
Hydrolysis is a persistent yet gradual process, crucial for maintaining CO₂ at a near-equilibrium state.

The process's intensity increases with rising temperature (T), increased precipitation (P, linked to T and atmospheric CO₂ content), and robust vegetation growth (related to T and P).

It is often referred to as the Earth's "thermostat."



A



B

What does the silicate weathering pump do to regulate the climate?

What does the silicate weathering pump do to regulate the climate?



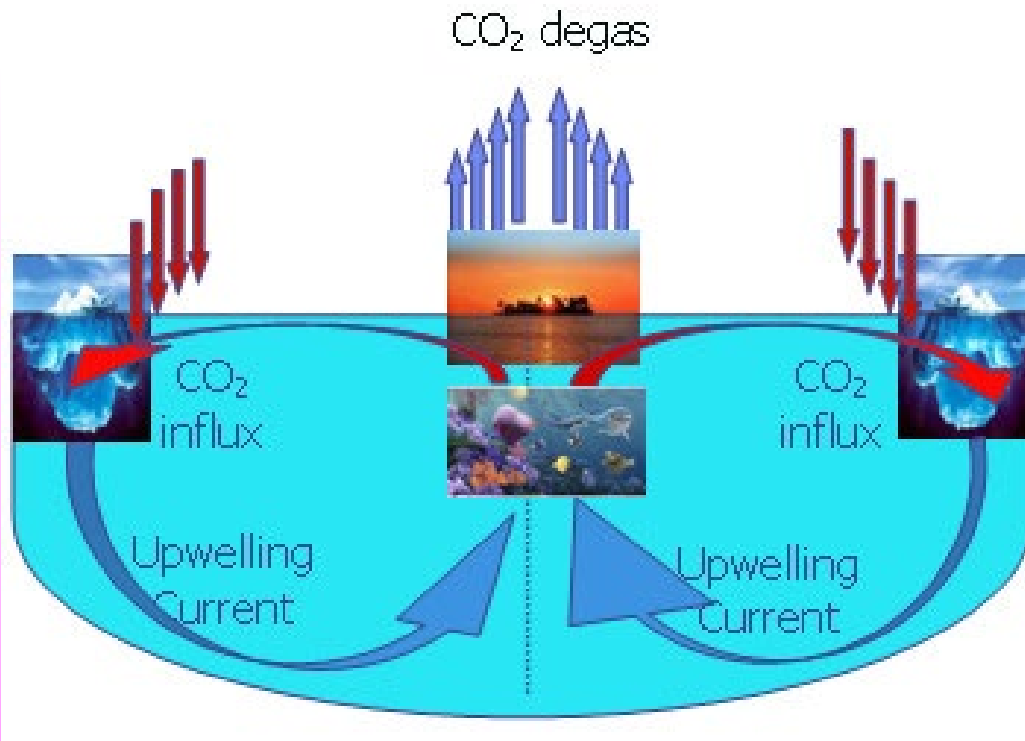
- 1 Increases carbon dioxide (CO₂) levels
- 2 Decreases CO₂ levels in the atmosphere
- 3 Enhances methane (CH₄) emissions
- 4 Cools the atmosphere

<https://app.wooclap.com/events/PCCM24/0>

OCEAN-ATMOSPHERE EXCHANGES OF CARBON

The (rapid) carbon exchanges between oceans and the atmosphere exclusively involve CO_2 . These exchanges encompass the outflow of CO_2 from the ocean to the atmosphere (degassing) and the inflow of CO_2 from the atmosphere to the ocean (influx). The solubility of CO_2 in the oceans depends on ocean water temperature, salinity, and atmospheric pressure.

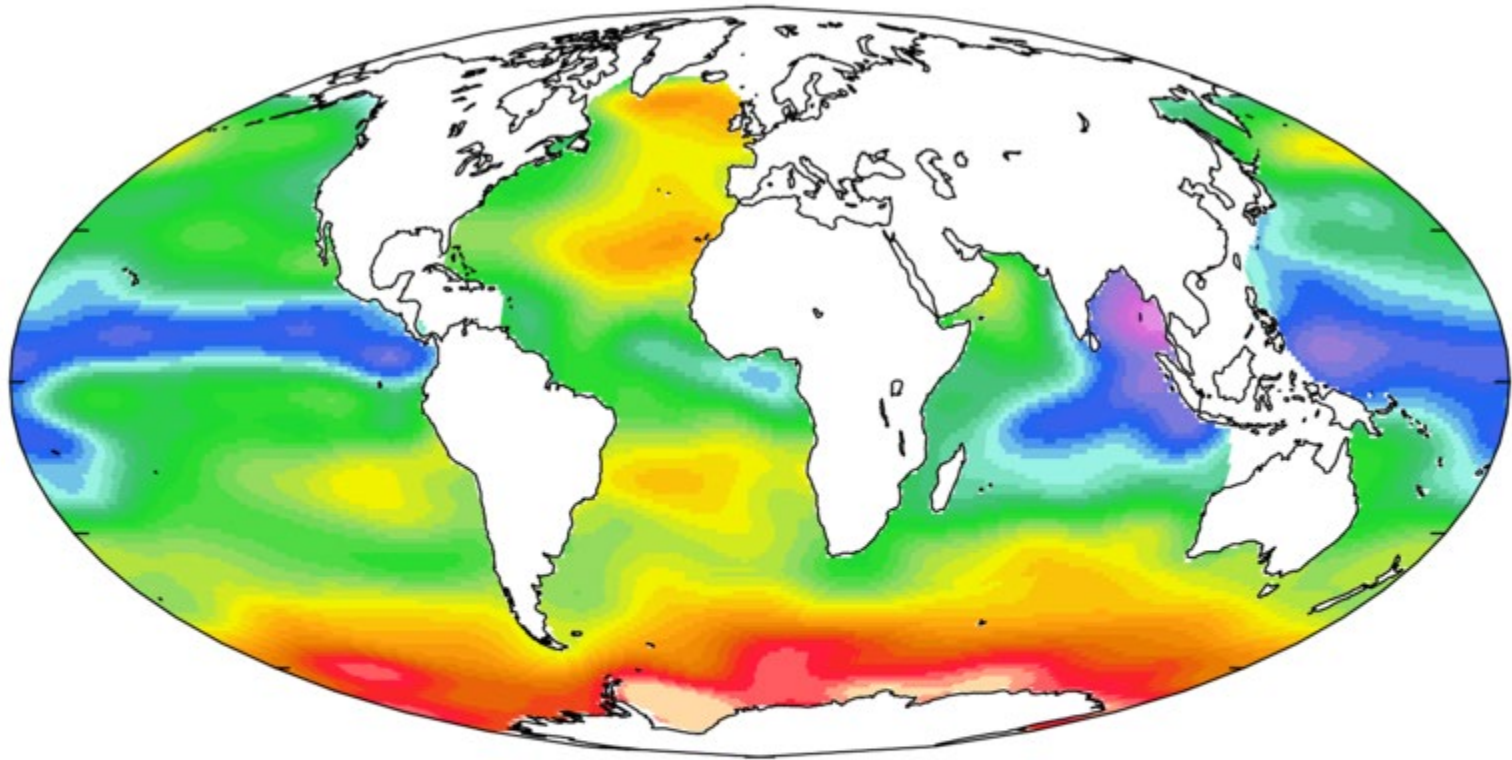
SOLUBILITY PUMP



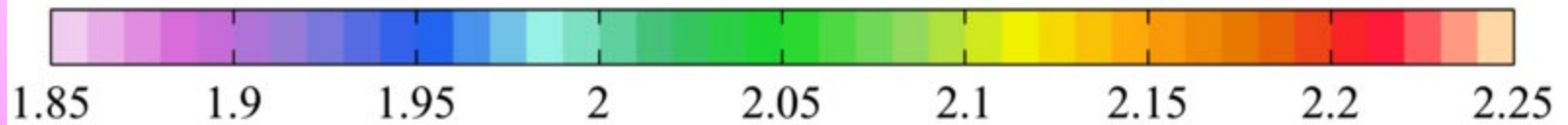
CO_2 is released to the atmosphere (*degas*) in tropical upwelling areas, where cold, CO_2 -rich waters emerge at higher temperatures.

CO_2 is absorbed (*influx*) in polar regions, where waters are cold and CO_2 is more soluble.

DISTRIBUTION OF DIC IN SURFACE WATERS



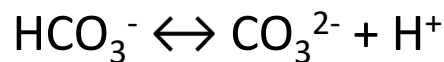
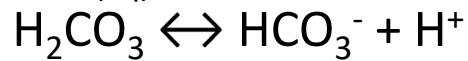
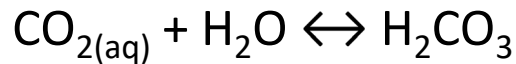
Present day sea-surface DIC [mol C m⁻³]



Solubility pump and ocean acidification

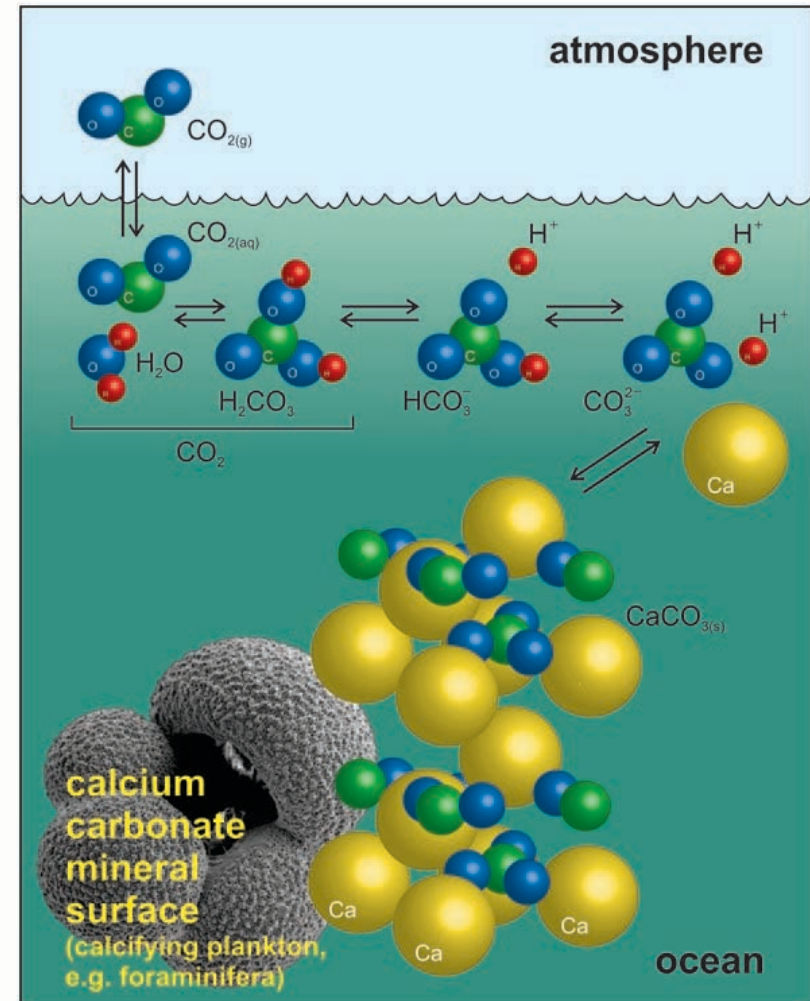
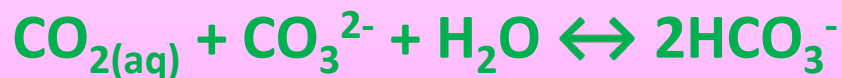
Absorption and release of CO_2 caused by changes in CO_2 solubility is called “solubility pump”.

CO_2 enters in sea waters from the atmosphere

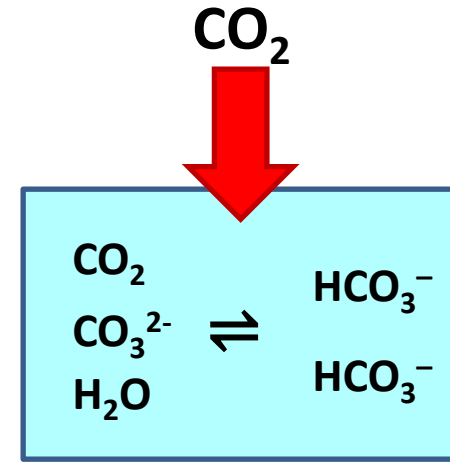
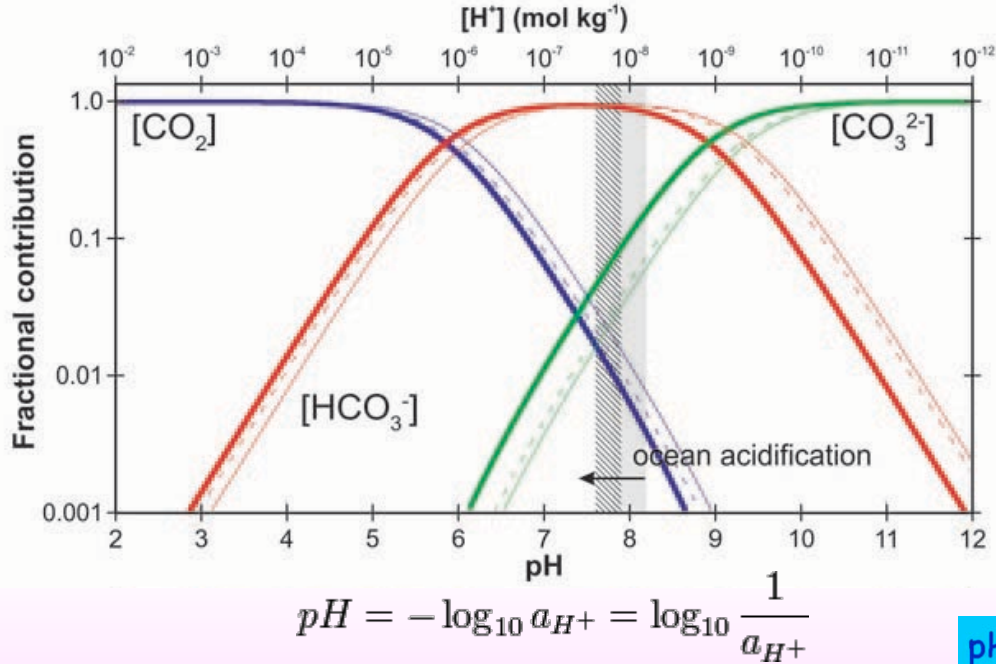


carbonic acid
bicarbonate
carbonate

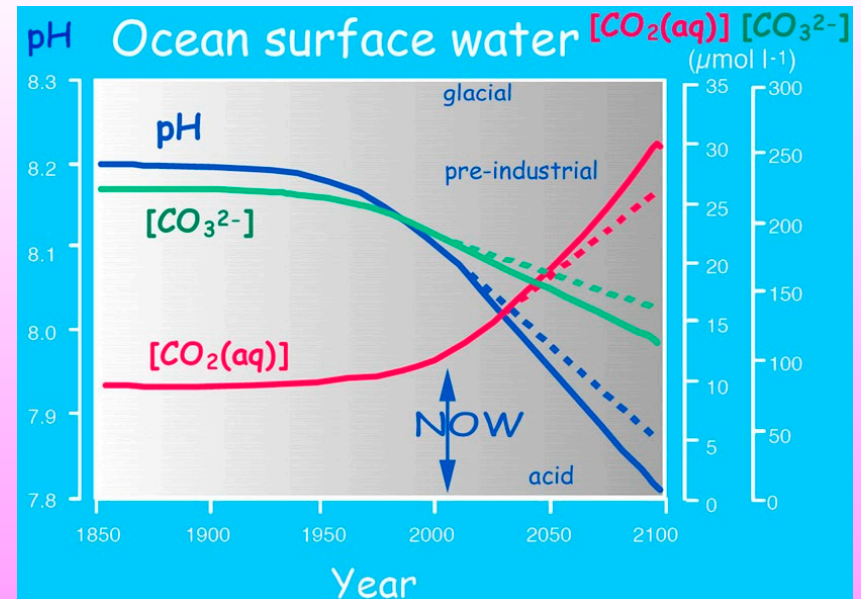
CO_2 dissolves in the water but not completely so that the amount of CO_3^{2-} and H^+ is less than expected because of the dissolution reaction that tends to balance the equation



Solubility pump and ocean acidification



The human-caused release of CO₂ into the atmosphere is partially taken up by the oceans, leading to an increase in their acidity.



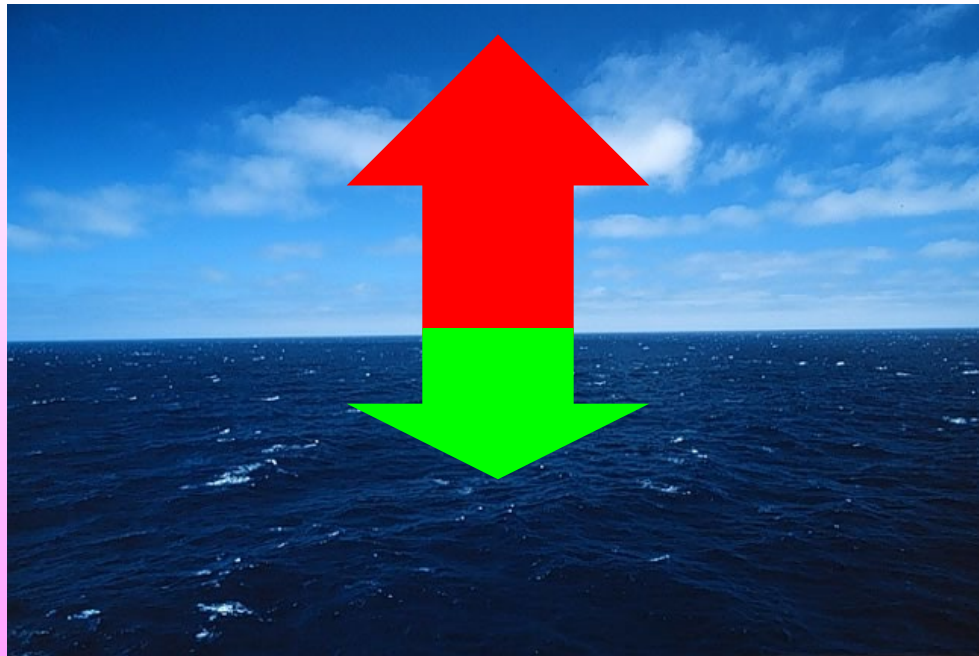
Ocean and anthropogenic CO₂

Annual emission of anthropogenic CO₂ : 6-7 Gt C

Annual absorption of CO₂ by the oceans: 2 Gt C

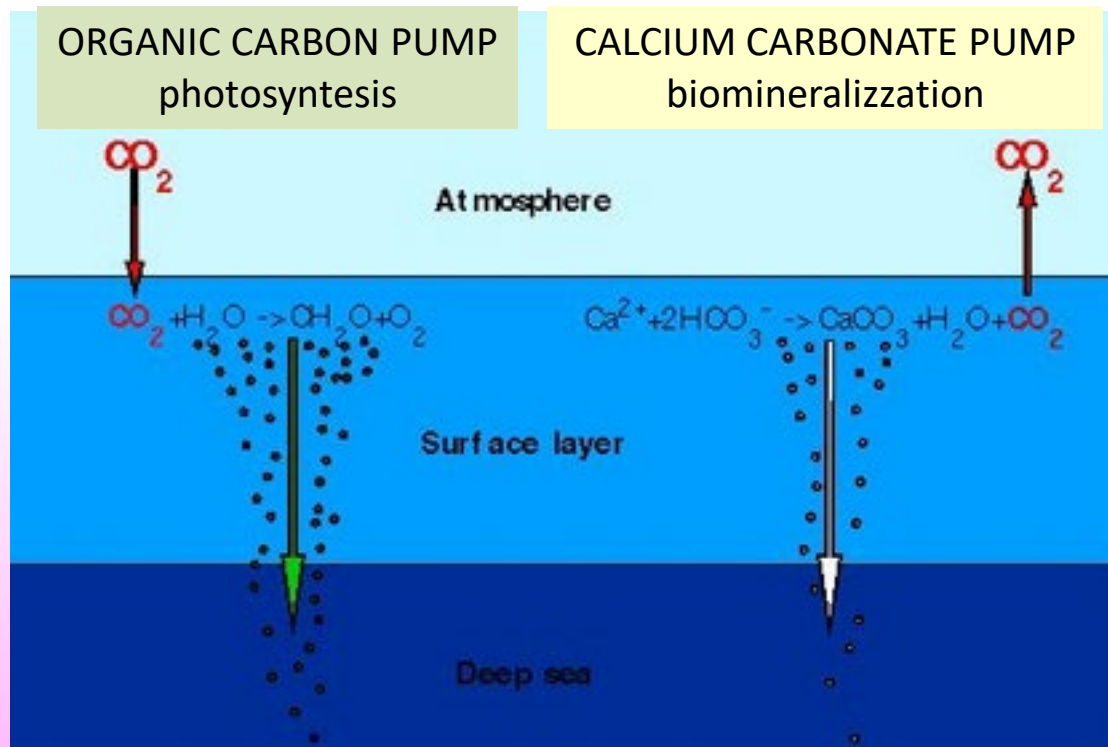
C input into the atmosphere from 1751: 305 Gt C

C absorbed by the oceans from 1751: 118 Gt C



BIOLOGICAL PUMPS

The ocean exchanges (rapidly) CO_2 with the atmosphere thanks to physical/chemical processes related to the solubility pump and the biological pumps.



The balance between these two mechanisms is crucial to understand the C fluxes between the atmosphere and the ocean.

1) organic carbon pump:

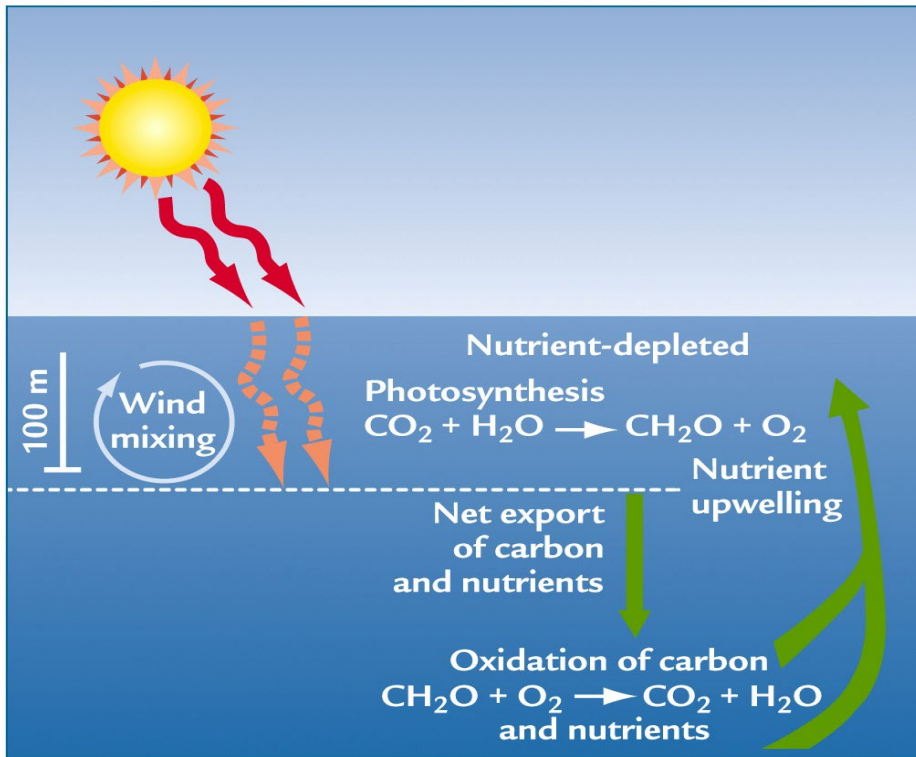
Photosynthesis utilizes carbon (C) to create organic matter (and O_2), which eventually sinks to the deep ocean, resulting in a net CO_2 sequestration.

2) carbonate carbon pump:

Certain organisms utilize carbon (C) to form their tests or shells made of calcium carbonate (CaCO_3). This chemical process releases and stores CO_2 , known as the carbonate counter pump.

ORGANIC CARBON PUMP & C_{ORG} REGENERATION

.. phytoplankton, the basis of the food chain, use C by "capturing" it from the TDIC (operating a strong isotope fractionation) and determines the biological productivity in an area (limiting factors → nutrients: P, N, Si, Fe etc.) .



When phytoplankton die, decompose, with only a small portion reaching the ocean floor.

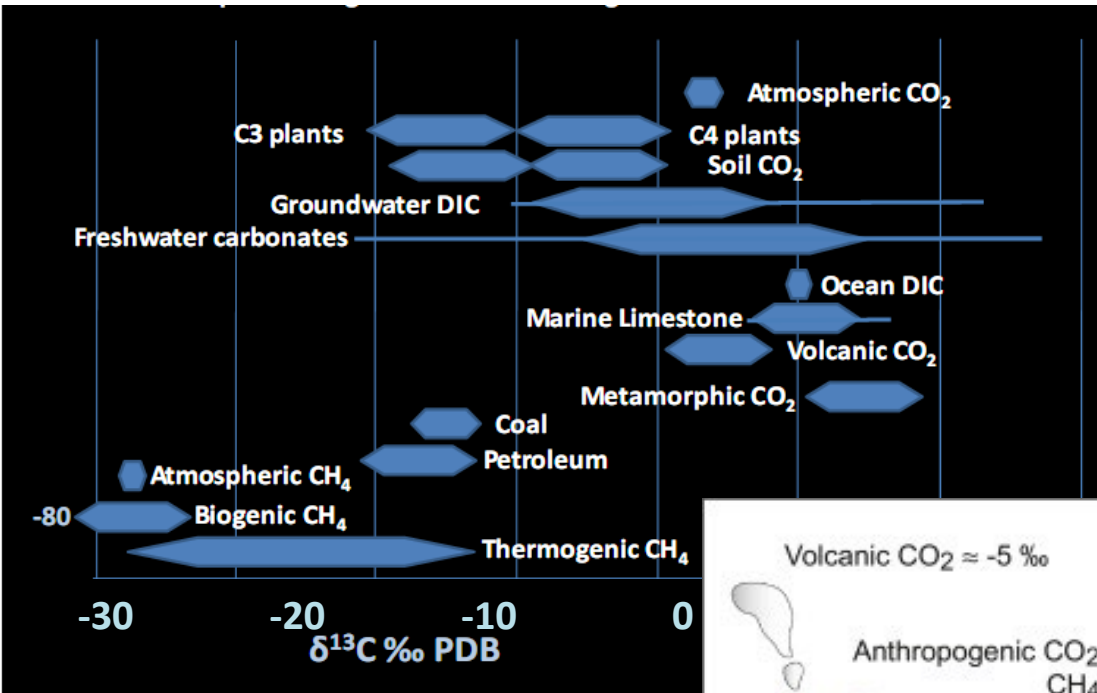
Over 95% of the carbon produced in photosynthesis is annually recycled in surface waters:

Regenerative Primary Production

Bacteria play an important role, both in the photic and aphotic zone, in degrading / transforming organic matter into inorganic and nutrients so that they can be reused.

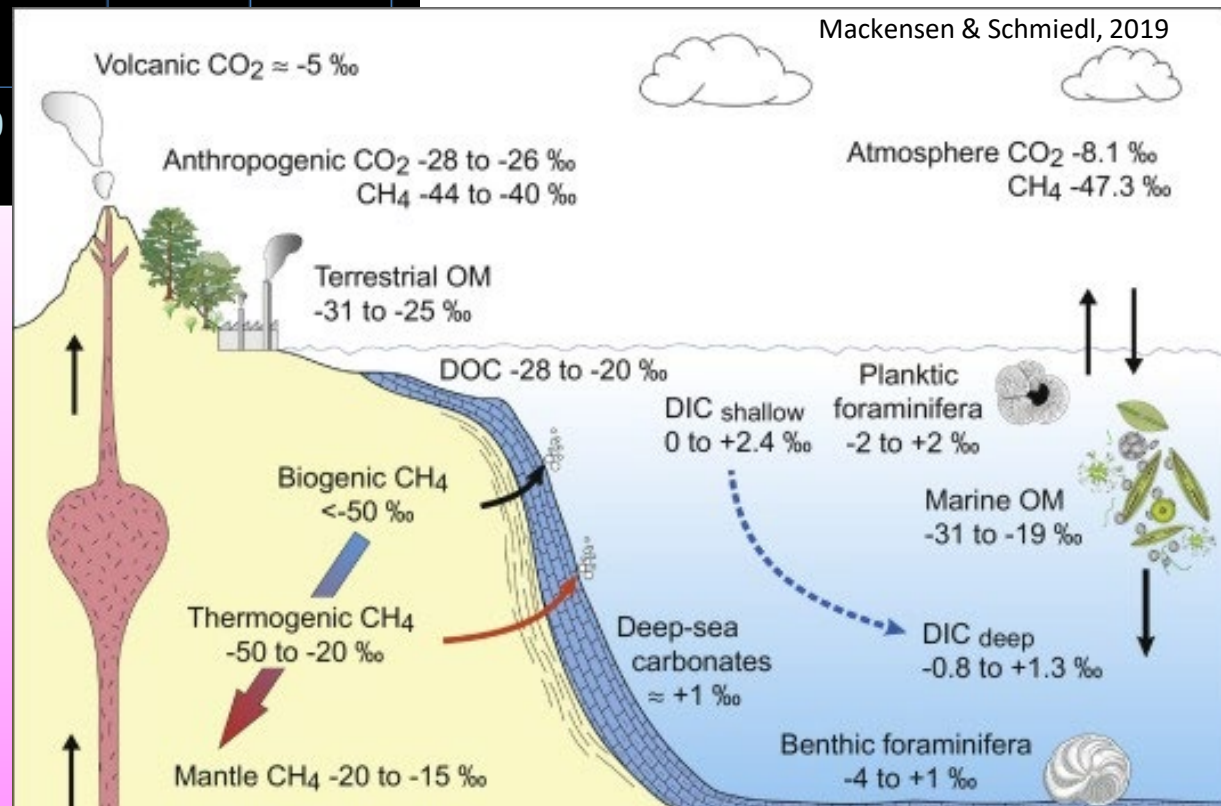
CARBON ISOTOPES IN MODERN OCEANS

VARIATIONS IN CARBON ISOTOPES



The $\delta^{13}\text{C}$ of numerous natural carbon compounds varies widely.

The variability of $\delta^{13}\text{C}$ largely depends on the isotope fractionation that occurs during photosynthesis (and bacterial chemosynthesis).



$\delta^{13}\text{C}$ VARIATION IN THE OCEANS

$\delta^{13}\text{C}$ in the TDIC in the oceans varies over space and (geological) time. The global mean value of $\delta^{13}\text{C}$ of the TDIC is currently ca. 0 but varies if observed over a long period (such as $\delta^{18}\text{O}$).

In modern ocean, these variations depend on:

1. **Biological productivity**

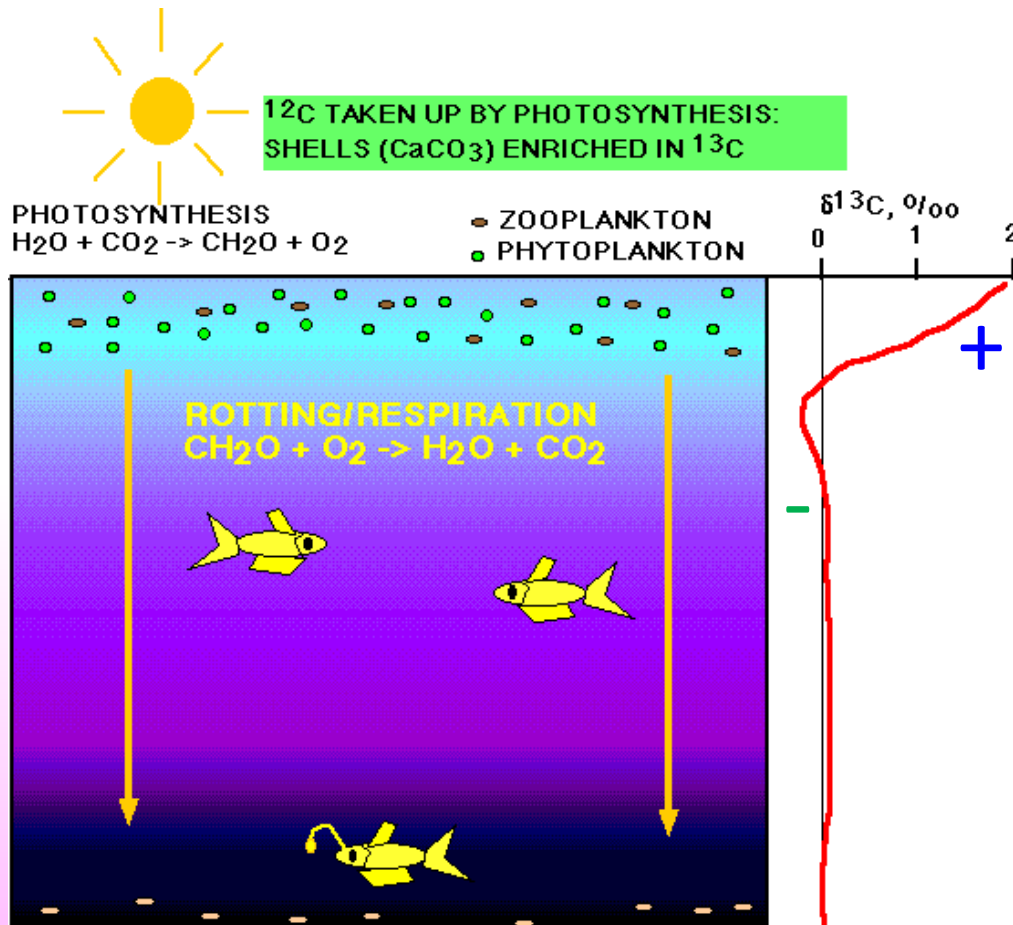
A) the prevalence of photosynthesis processes (photic zone) or breathing (deep water) => vertical gradient;

B) local conditions of biological productivity => regional gradient;

2. **ocean circulation** => thermoaline circulation;

3. **exchanges between reservoirs**

$\delta^{13}\text{C}$ "VERTICAL" GRADIENT IN THE OCEAN -1



SHALLOW WATERS

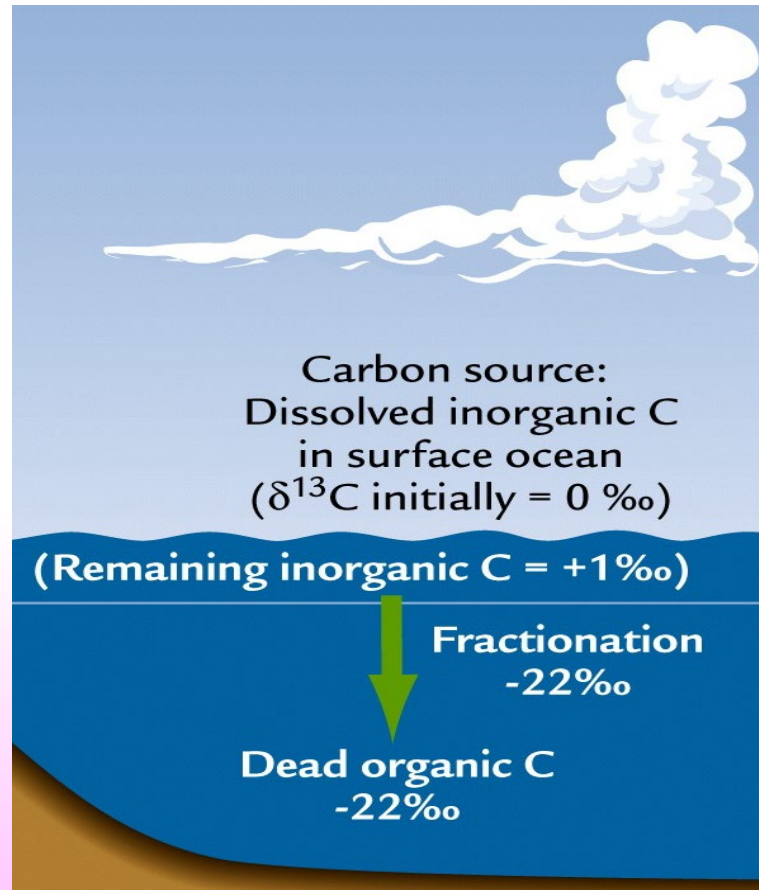
Photosynthesis in the photic zone produces assimilation of ^{12}C by phytoplankton and, therefore, a strong enrichment in ^{13}C in the DIC of surface waters, which commonly has values of $\delta^{13}\text{C}$ between **+1 and +3 ‰**.

DEEP WATERS

The $\delta^{13}\text{C}$ values of the DIC in deep waters are "lighter" because during the respiration and oxidation (decomposition) processes the ^{12}C previously segregated in the organic matter is released (in form of CO_2)

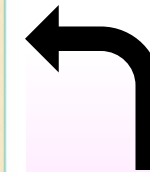
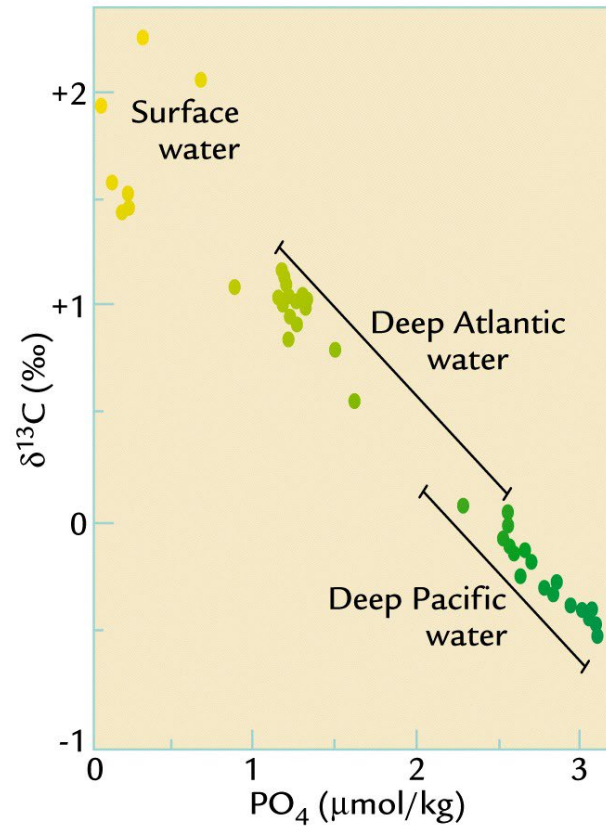
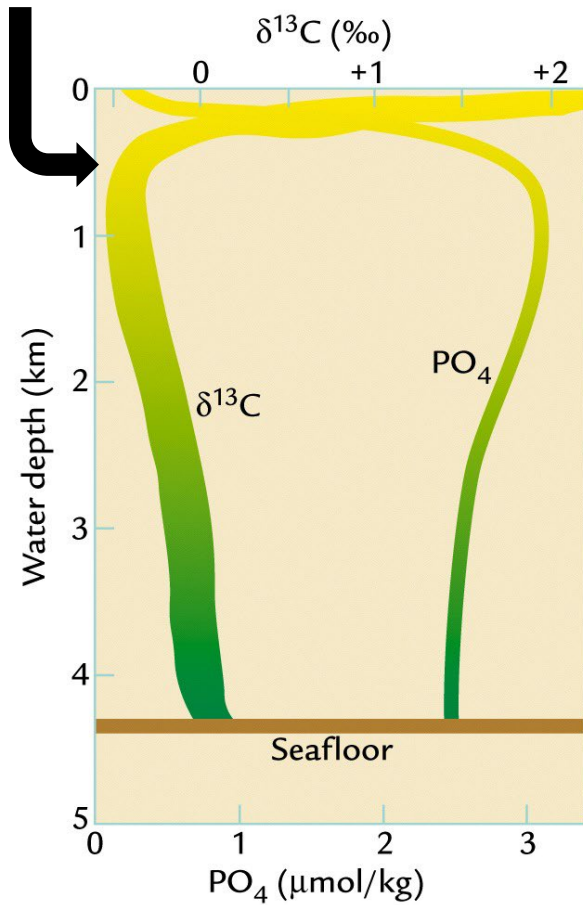
If we consider the entire ocean, the **average $\delta^{13}\text{C}$** of the TDIC (Total Dissolved Inorganic Carbon) is around **0 ‰**.

$\delta^{13}\text{C}$ VARIATION IN THE OCEANS



N.B. The mechanisms of photosynthesis of marine phytoplankton are still unclear, but we know that the $\delta^{13}\text{C}$ of organic matter in marine phytoplankton varies between -10 and -31 ‰ (commonly between -17 and -22 ‰).

$\delta^{13}\text{C}$ "VERTICAL" GRADIENT IN THE OCEAN -2

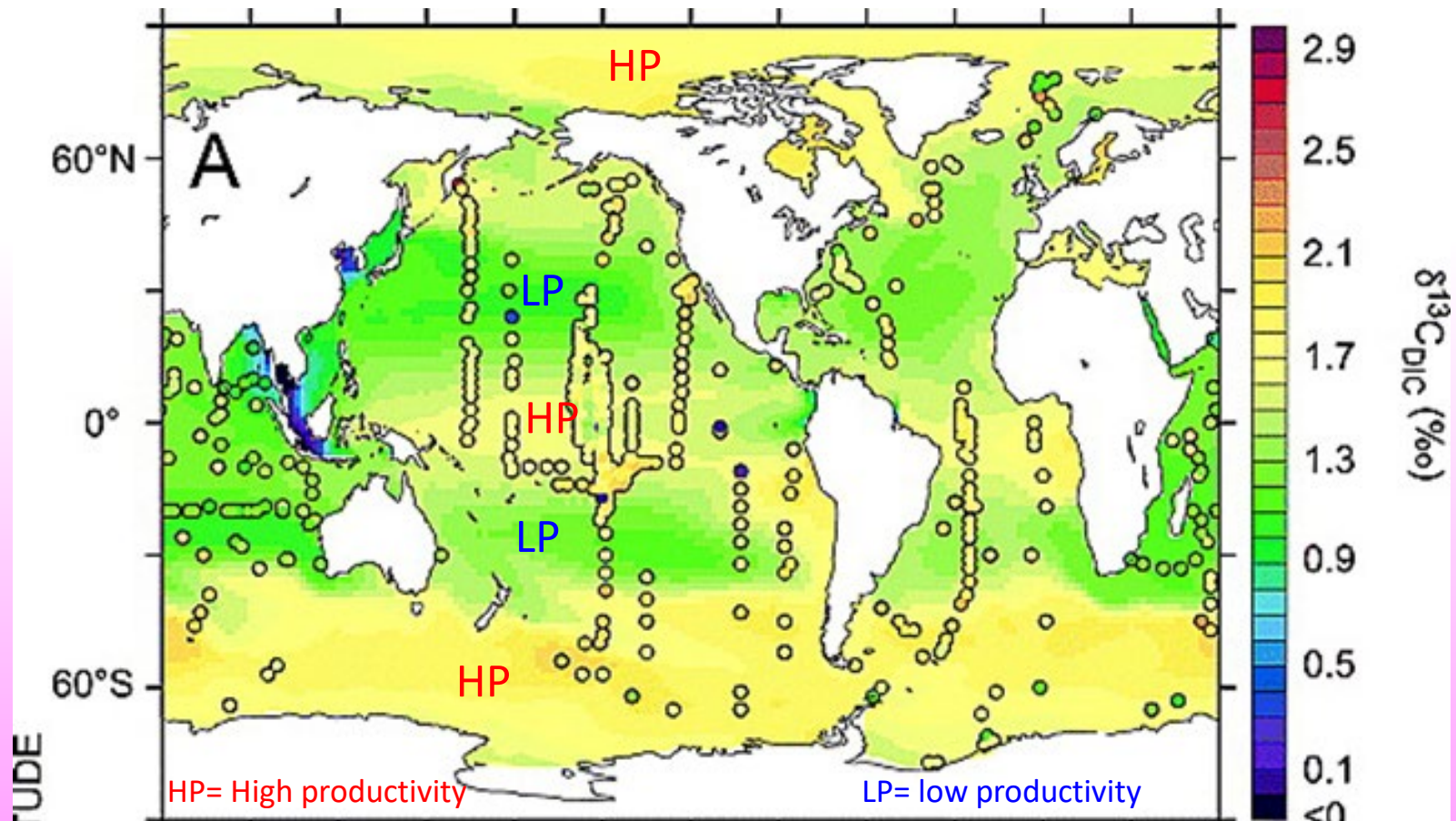


WATER IMPRINTING
The bottom waters of the oceans are formed at high latitudes. Their $\delta^{13}\text{C}$ represents a fingerprint.

$\delta^{13}\text{C}$ "REGIONAL" GRADIENT

REGIONAL GRADIENT (horizontal gradient)

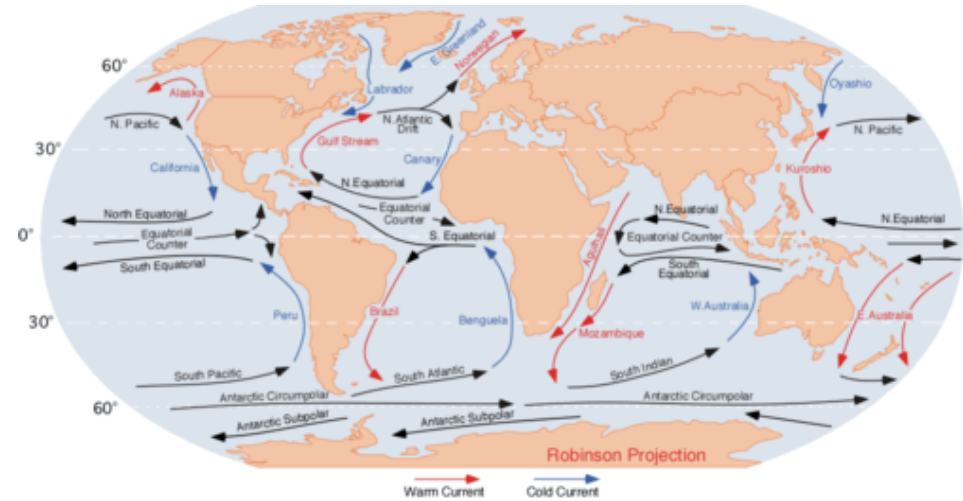
Biological productivity and, therefore, the intensity of photosynthesis, varies greatly in different areas depending on the availability of nutrients. At the same time, $\delta^{13}\text{C}$ values vary in the surface waters of the oceans, which will be heavier in the areas of high productivity.



OCEANIC CIRCULATION - 1

SURFACE CIRCULATION

We mean the horizontal motion of the surface water mass (or surface currents) due to the combined action of gradient currents (pressure and density) and drift (winds).

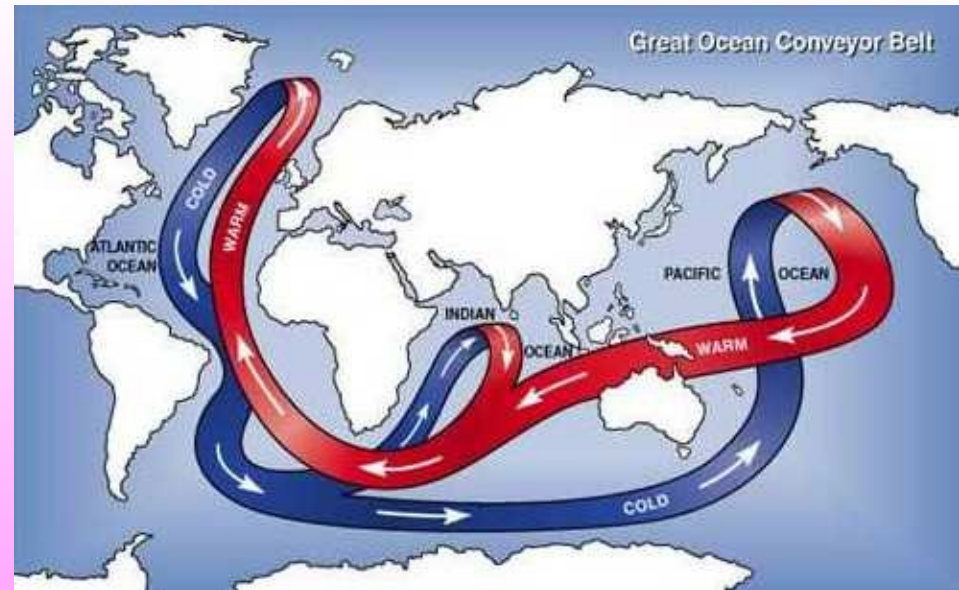


SURFACE WATERS CURRENTS

THERMOALINE CIRCULATION

we mean the global ocean circulation caused by the density variation of the water masses. Density depends on temperature (thermo-), salinity (-aline) and water pressure.

$$\rho \text{ (DENSITY)} = \text{mass/volume} = m/V$$

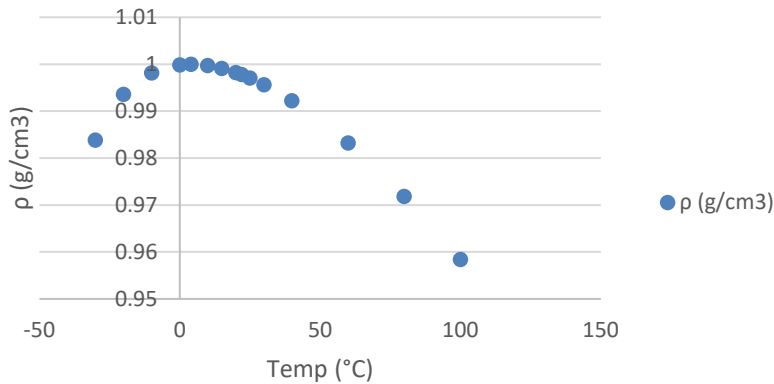


DEEP WATER CURRENTS

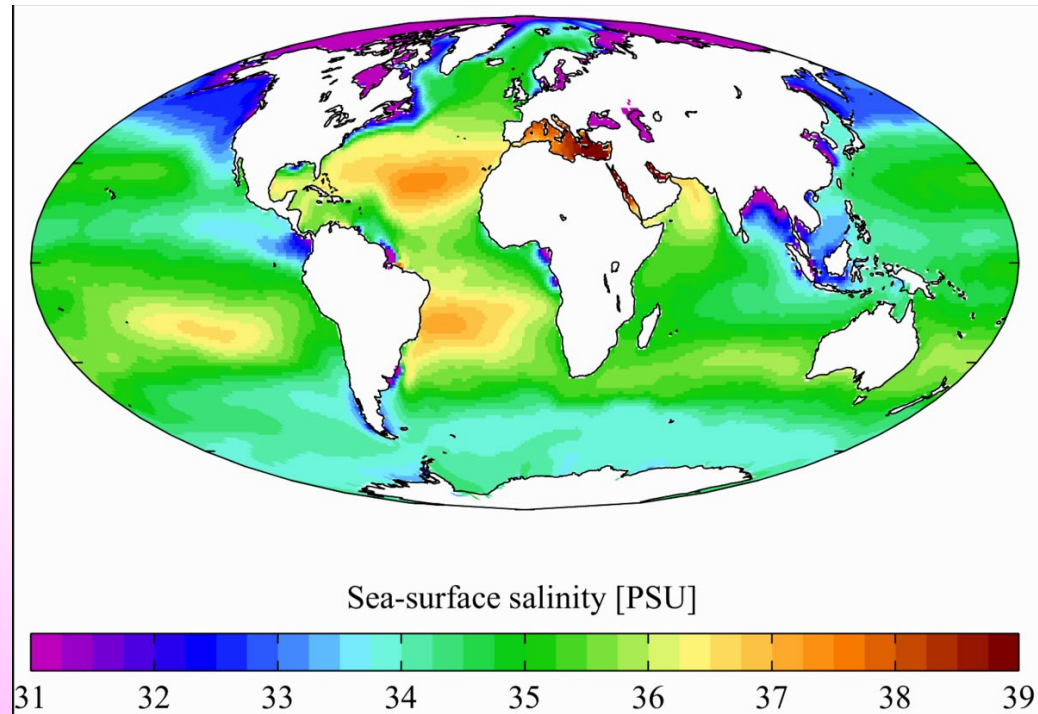
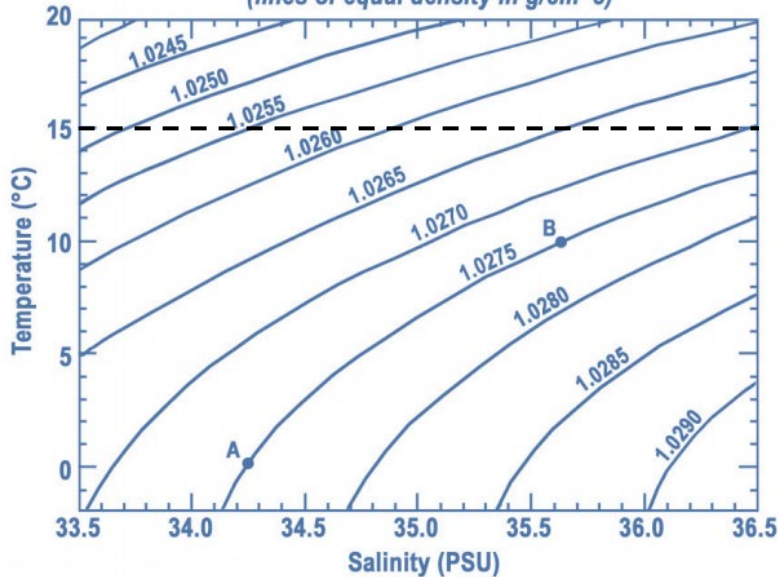
OCEANIC CIRCULATION - 2

$$\rho \text{ (densità)} = \text{mass/volum} = m/V$$

ρ (g/cm³) water



Temperature-Salinity Diagram
(lines of equal density in g/cm³)



OCEANIC CIRCULATION - 3

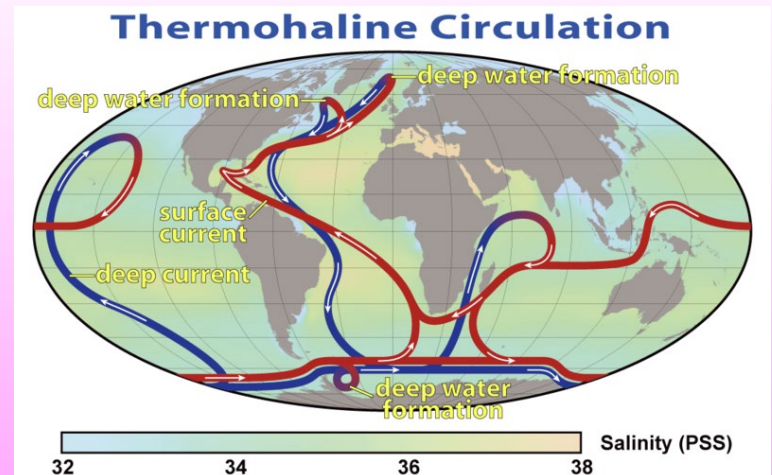
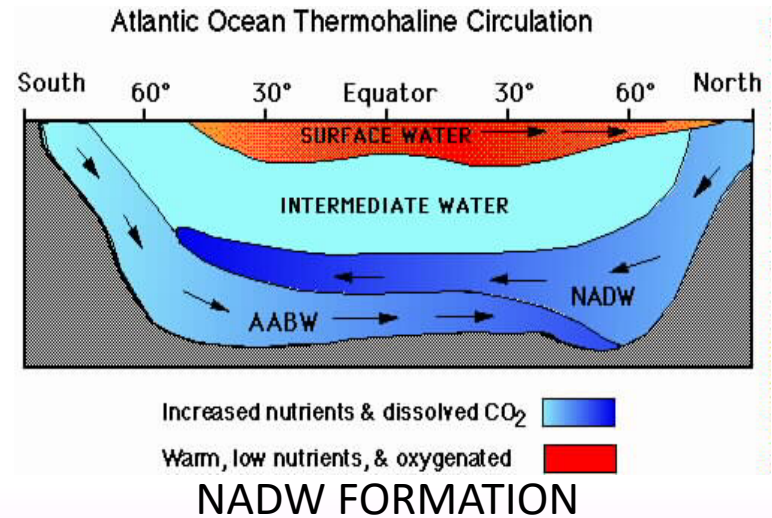
THE FORMATION OF A MASS OF WATER

A mass with typical values of temperature and salinity is formed when the water is subjected to specific climatic conditions for a period of time sufficient to impart the characteristics that will make it recognizable even when it spreads in places other than those of formation.

THE FORMATION OF THE NADW AND THE DEEP CIRCULATION

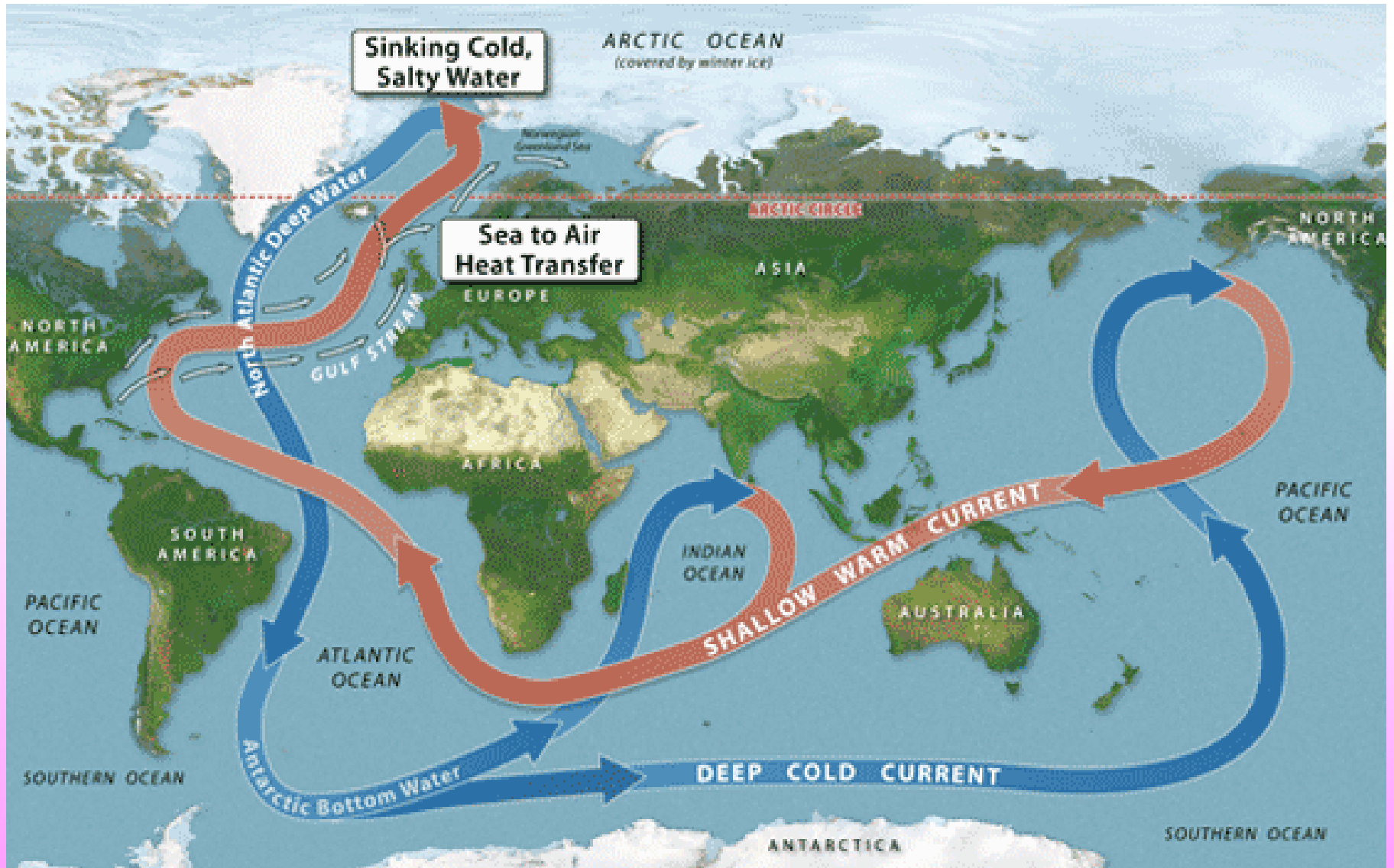
At high latitudes (SE Greenland and Iceland) the water sinks, both due to the low temperature and the high salinity caused by the formation of the ice pack.

Moving towards the equator, the bottom water decreases its density interacting with other waters and tends to rise, particularly south of the Indian Ocean.



OCEANIC CIRCULATION - 4

DEEP WATER CIRCULATION – CONVEYOR BELT



$\delta^{13}\text{C}$ and OCEAN CIRCULATION: "OLD WATERS" vs "YOUNG WATERS"

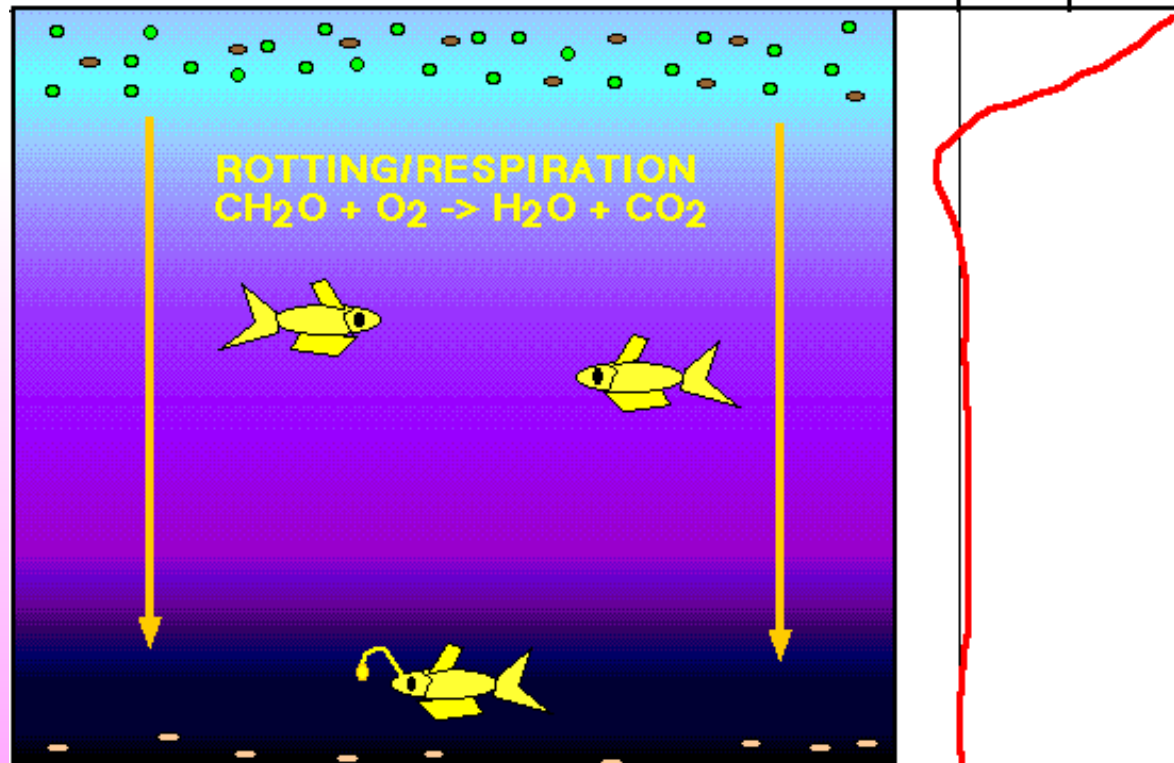


^{12}C TAKEN UP BY PHOTOSYNTHESIS:
SHELLS (CaCO_3) ENRICHED IN ^{13}C

PHOTOSYNTHESIS
 $\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{CH}_2\text{O} + \text{O}_2$

● ZOOPLANKTON
● PHYTOPLANKTON

$\delta^{13}\text{C}, \text{‰}$
0 1 2



$\delta^{13}\text{C}$ and OCEAN CIRCULATION: "OLD WATERS" vs "YOUNG WATERS"

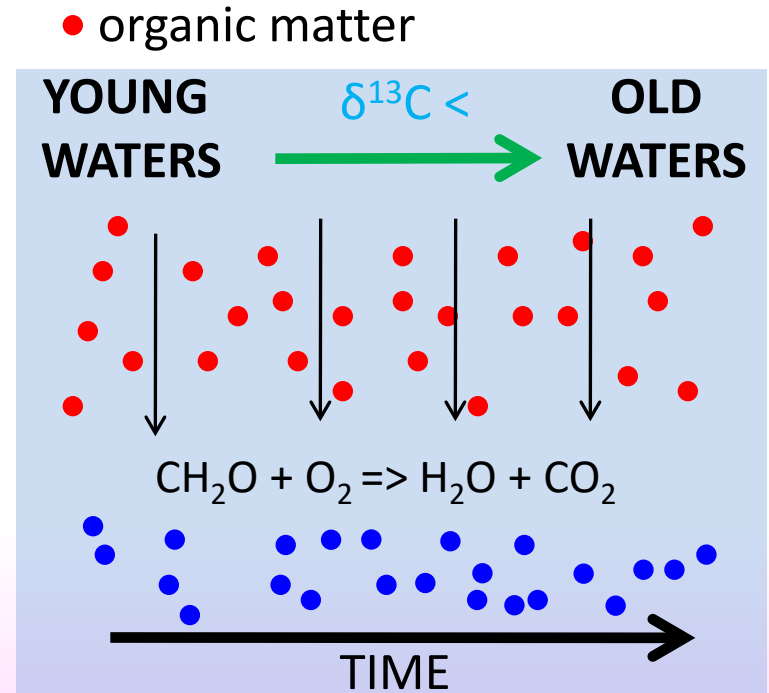
During its path, a water mass continues to receive organic matter, which oxidizes producing CO_2 enriched in ^{12}C .

OXIDATION OF ORGANIC MATTER



The $\delta^{13}\text{C}$ of the deep water TDIC varies according to age, $\delta^{13}\text{C} <$ with increasing age.

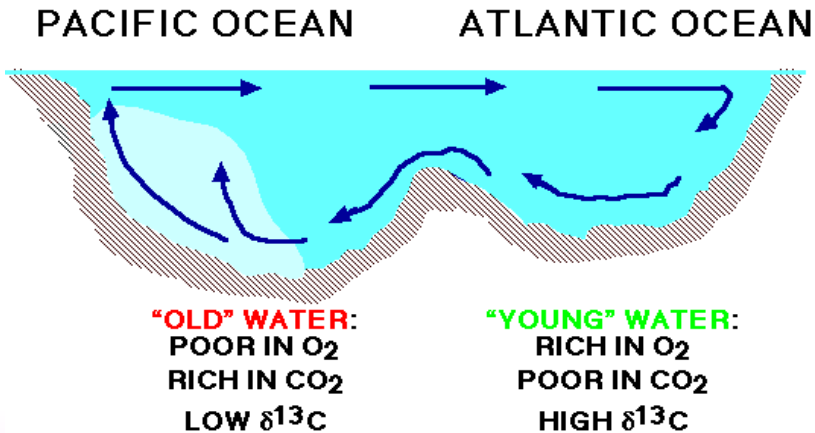
$\delta^{13}\text{C}$ of northern Pacific Ocean (old waters) is lighter of ca. 1‰ compared with that of the Atlantic Ocean (young waters).



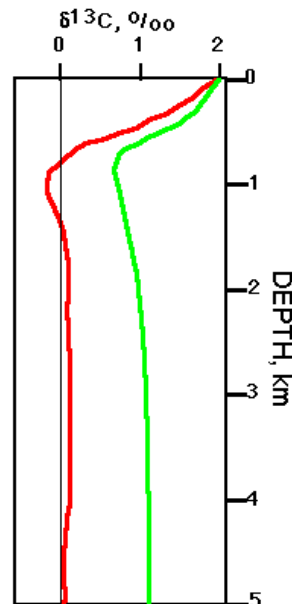
Organic matter
oxidation/decomposition
 ^{12}C release

Lightening of $\delta^{13}\text{C}$

$\delta^{13}\text{C}$ and OCEAN CIRCULATION: "OLD WATERS" vs "YOUNG WATERS"



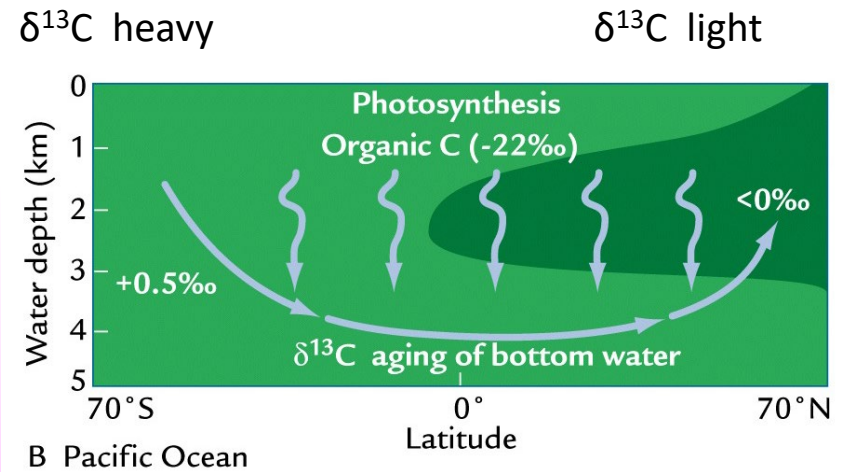
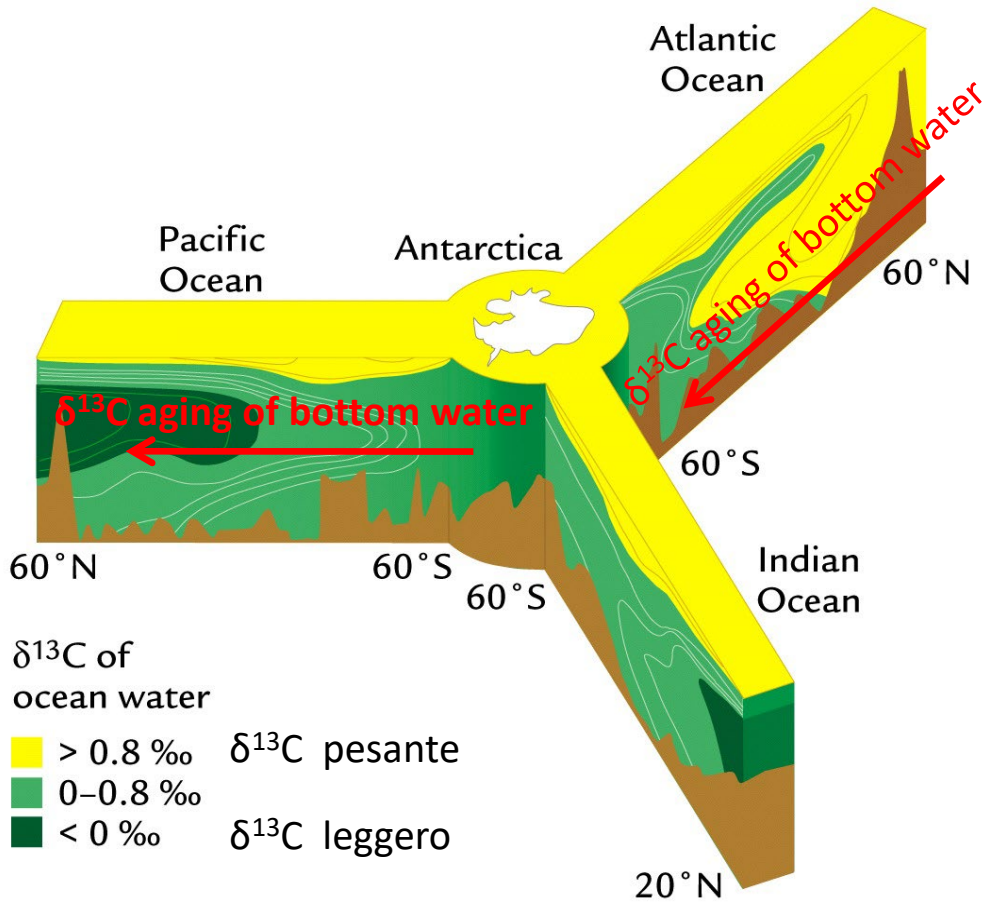
In modern oceans there is a marked difference between the $\delta^{13}\text{C}$ of the TDIC of the deep Atlantic waters ("young" waters) and the $\delta^{13}\text{C}$ of the Pacific TDIC ("old" waters).



The **"old"** deep waters are characterized by:

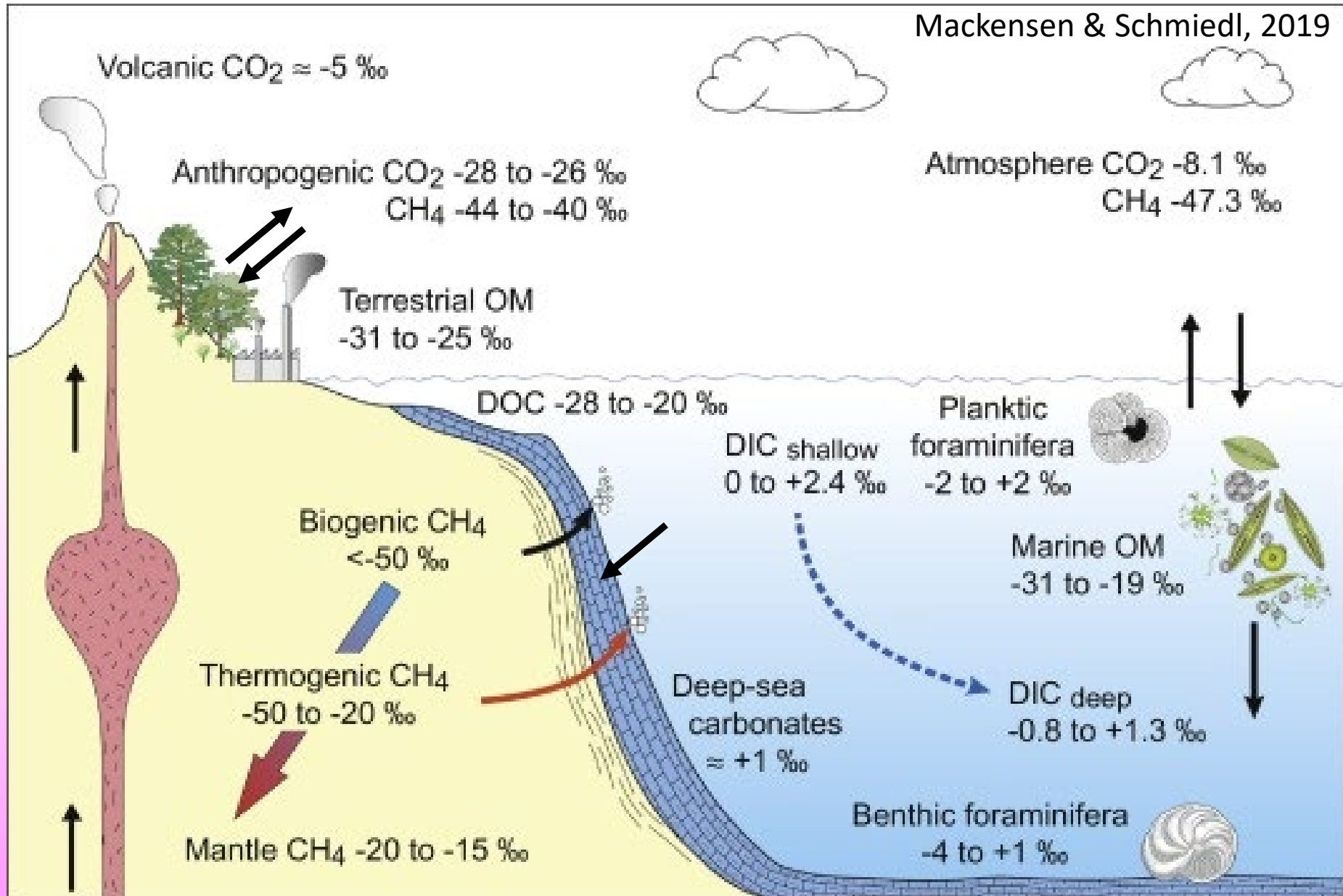
- **Lighter $\delta^{13}\text{C}$ values of the TDIC**
- **a lower content of O_2 ;**
- **a higher content of CO_2 and nutrients (nitrates, phosphates and silicates).**

$\delta^{13}\text{C}$ IN THE MODERN DEEP OCEAN



3. Exchanges between reservoirs and $\delta^{13}\text{C}$

Mackensen & Schmiedl, 2019



$\delta^{13}\text{C}$ IN THE OCEAN: A SUMMARY

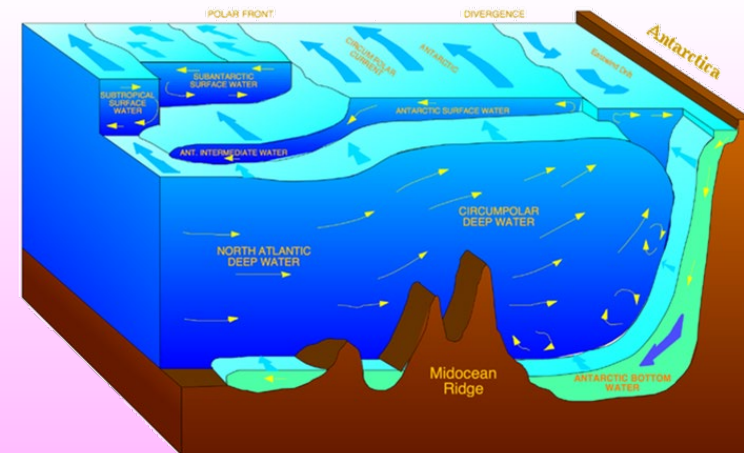
There are short-term and long-term variations. For example, exchanges between the upper ocean and the atmosphere are almost immediate (a few years), while the exchanges between the upper ocean and the deep ocean take place over hundreds of years (ocean circulation).

The variations $\delta^{13}\text{C}$ depend on:

- 1) biological productivity: a) high productivity \rightarrow "heavy" values of $\delta^{13}\text{C}$ water
b) vertical gradient (photosynthesis / oxidation)
c) horizontal gradient
- 2) General ocean circulation (e.g., waters "Young" and "old" waters)
- 3) Exchanges between reservoirs (the intensity of exchanges is variable in space and time)

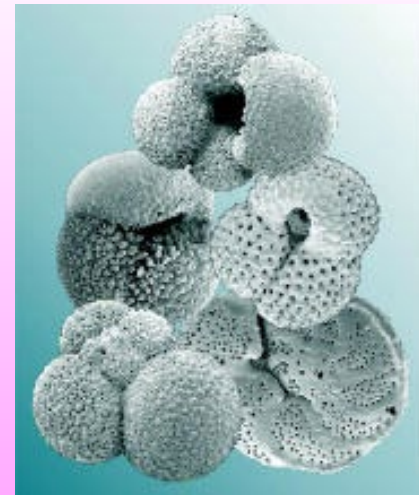
Example:

- Mean ocean deep water $\delta^{13}\text{C}$: 0.00 ‰
- Mean ocean surface water $\delta^{13}\text{C}$: 2.00 ‰
- NADW $\delta^{13}\text{C}$: 1.10 ‰ (cold and salty) - AABW $\delta^{13}\text{C}$: 0.30‰ (cold and salty)
- Present gradient of $\delta^{13}\text{C}$ between N Atlantic and Pacific:
ca. 1.2‰ (*aging* effect+ *mixing* effect between AABW and NADW).



CARBON ISOTOPES IN THE GEOLOGICAL PAST

Carbon isotopes can be studied in different geological materials: petroleum, bones, plant material and carbonates. Carbonate analyzes are carried out on single fossils, on total rock (bulk carbonate) and / or on nodules present within paleosols. *We will focus on microfossils and bulk carbonate.*



$\delta^{13}\text{C}$ in CARBONATES

TEMPERATURE

Unlike what happens for oxygen, $\delta^{13}\text{C}_{\text{carb}}$ is **virtually unaffected by changes in temperature** (approx. 0.035 ‰ per 1°C).

FRACTIONATION

The precipitation of carbon in carbonates (calcite, aragonite, dolomite, etc., not in organic matter) **does not involve a significant isotopic** fractionation with respect to the isotopic composition of the inorganic C used (CO_2 , CO_3^{2-} e HCO_3^-).

The $\delta^{13}\text{C}$ of carbonates precipitated in the oceans is very similar (a bit higher) to the $\delta^{13}\text{C}$ of the Total Dissolved Inorganic Carbon (TDIC) of the environment (water) where the carbonates themselves were formed.



The $\delta^{13}\text{C}$ of marine carbonates (e.g., foraminiferal shells) **is a "direct proxy" of the $\delta^{13}\text{C}$ of the TDIC dissolved in the water where the carbonates** (e.g., the shells of foraminifera) are formed.

$\delta^{13}\text{C}$ FORAMINIFERAL GRADIENTS

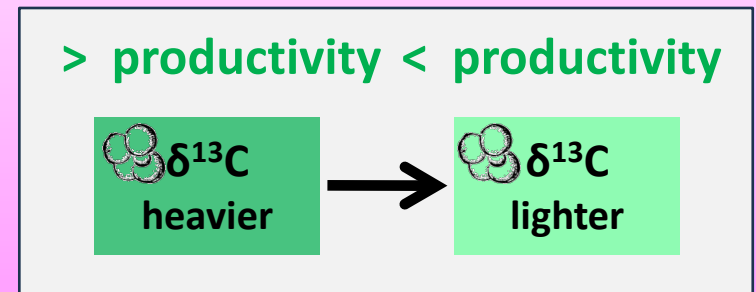
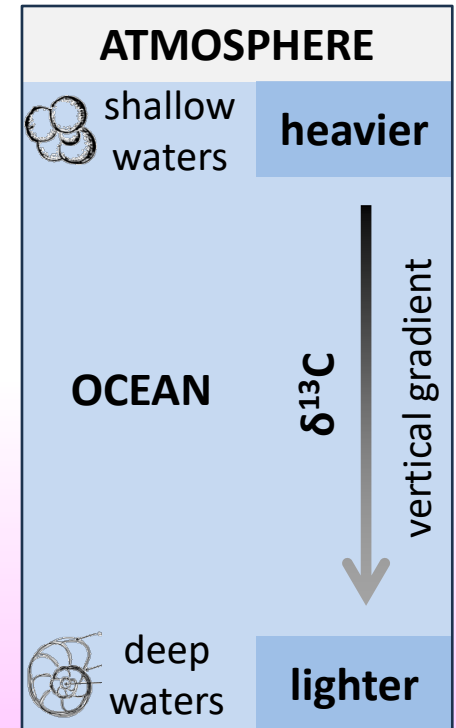
If the $\delta^{13}\text{C}$ of oceanic carbonates (e.g. foram shells) closely matches the $\delta^{13}\text{C}$ of the surrounding total dissolved inorganic carbon (TDIC), it signifies minimal isotopic alteration during carbonate fractionation.

VERTICAL GRADIENT

Due to the vertical gradient in the $\delta^{13}\text{C}$ of water, **planktonic organisms** living in the photic zone **incorporate isotopically heavier carbon** into their carbonate shells by utilizing dissolved inorganic C, primarily HCO_3^- . This results in "surface dwellers" planktonic foraminifera having a $\delta^{13}\text{C}$ in their CaCO_3 shells that is heavier, similar to that of surface water TDIC. On the other hand, **benthic foraminifera's shell calcite contains lighter $\delta^{13}\text{C}$** , reflecting that of deep water TDIC. (eep water TDIC).

HORIZONTAL GRADIENT

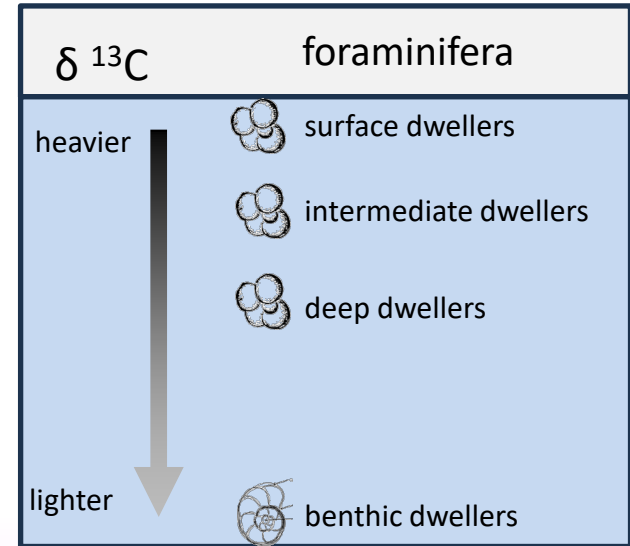
As a result of isotopic fractionation during phytoplankton production, an **increase in the $\delta^{13}\text{C}$ is evident in waters with greater productivity** (exceeding photosynthesis). This alteration is recorded in the CaCO_3 of surface-dwelling foraminifera.



PALEOECOLOGICAL APPLICATION - 1

RECONSTRUCTION OF THE ECOLOGY OF THE PLANKTONIC FORAMINIFERS OF THE PAST:

The same sample (= isotopic composition of the TDIC) will show $\delta^{13}\text{C}$ heavier for "surface dwellers" than for "intermediate dwellers" or "deep dwellers".

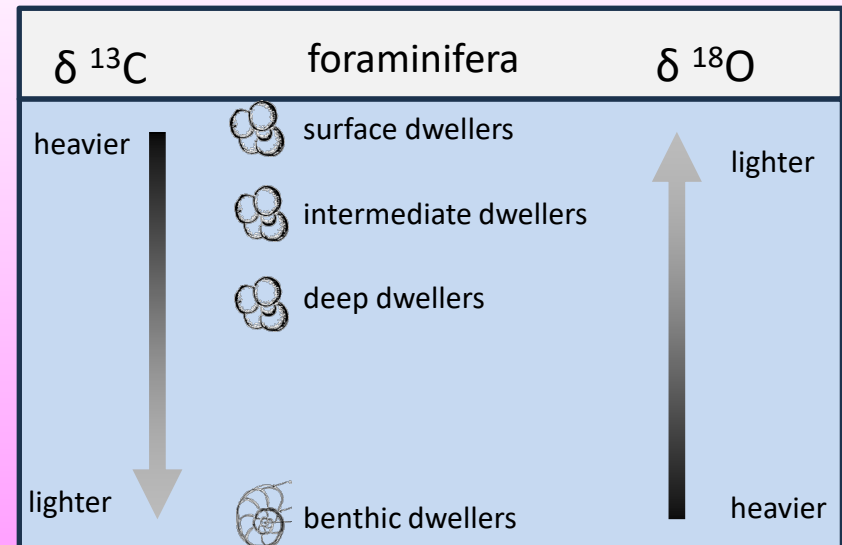


COMPARISON WITH THE $\delta^{18}\text{O}$ DATA:

The oxygen isotopes in the same sample are influenced by the $T^\circ\text{C}$ which is a function of depth:

"surface dwellers" (warmer waters) → lighter $\delta^{18}\text{O}$

"deep dwellers" (colder waters) → heavier $\delta^{18}\text{O}$



PALEOECOLOGICAL APPLICATIONS - 2

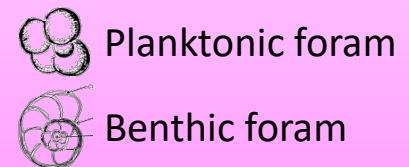
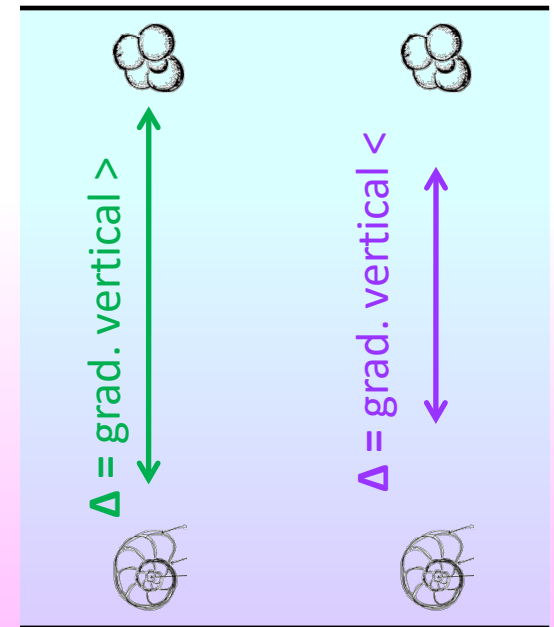
RECONSTRUCTION OF VERTICAL GRADIENTS (Δ) of $\delta^{13}\text{C}$ IN THE OCEANS OF THE PAST: INTENSITY OF BIOLOGICAL PUMP

This gradient is mainly a function of the productivity conditions in surface waters: the greater the number of plants and photosynthetic bacteria (i.e., the greater the biological productivity), the greater the ^{12}C "imprisoned" in the organic matter, which will be transported from the surface of the oceans at the bottom and incorporated in the sediments (biological pump), and the greater the ^{13}C incorporated in the shell of the planktonic foraminifera that precipitate CaCO_3 from the (surface) waters in which they live.

Benthic foraminifera live at the bottom of the oceans where productivity variations are more limited.

Therefore, the difference in $\delta^{13}\text{C}$ between planktonic and benthic is ultimately a proxy of the intensity of the "biological pump" of C which, in geological times, has a great importance on the global cycle of C (removes CO_2).

| | |
|-------------------------|-------------------------|
| $\delta^{13}\text{C} >$ | $\delta^{13}\text{C} <$ |
| high productivity | low productivity |



PALEOECOLOGICAL APPLICATIONS - 3

ISOTOPIC FRACTIONATION IN THE FOOD CHAIN

The carbon isotope values acquired during the primary production of organic matter propagate through the food chain.

The tissues of organisms will have an isotopic composition that will depend on the organic matter that that organism has fed on.

However, a further isotope fractionation occurs each time an organism feeds on. In other words, there is a "constant" offset between the $\delta^{13}\text{C}$ of food and the $\delta^{13}\text{C}$ of the body's tissues.

Examples:

1. In large modern mammals, tooth enamel has a heavier $\delta^{13}\text{C}$ (-14.5 ‰) than that of the food they eat (-26.5 ‰) (see next Fig.).
2. Populations that feed mainly on derivatives of maize (C4) (or beef, fed on maize) have a heavier isotopic footprint than populations that feed on rice, wheat or potatoes (C3). Note that the "isotopic footprint" of plants (C3 or C4) is transferred to the human teeth, albeit with a fractionation.

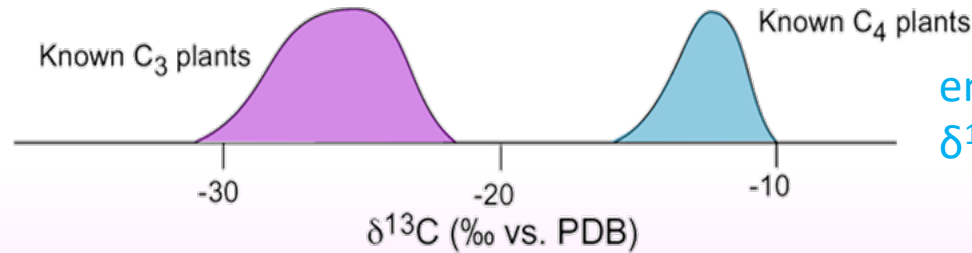
PALEOECOLOGICAL APPLICATION - 3

AUTOECOLOGY OF COMPLEX ORGANISMS (LARGE VERTEBRATES):

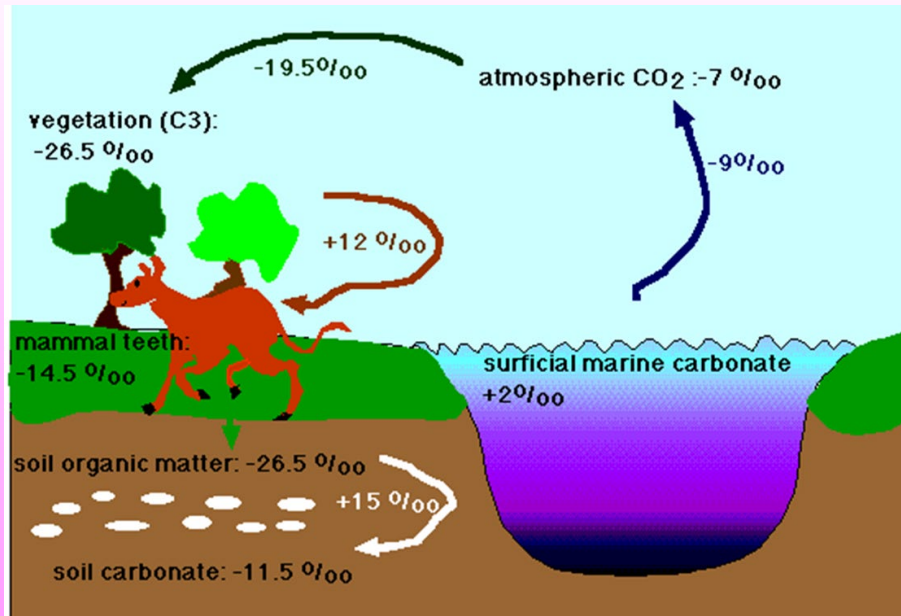
the $\delta^{13}\text{C}$ of their teeth is a function of the vegetables they have eaten. Carbon isotopes have been used to infer the paleo diet of large vertebrates: "Browsers" (browsers; e.g., giraffes) => isotopically lighter C3 plants. "Grazers" (grazers; e.g., wildebeest) => isotopically heavier C4 plants.

Isotopic result:

enriched in ^{12}C
 $\delta^{13}\text{C}$ lighter



enriched in ^{13}C
 $\delta^{13}\text{C}$ heavier



PALEOCEANOGRAPHIC APPLICATIONS - 1

PAST OCEAN CURRENT RECONSTRUCTIONS

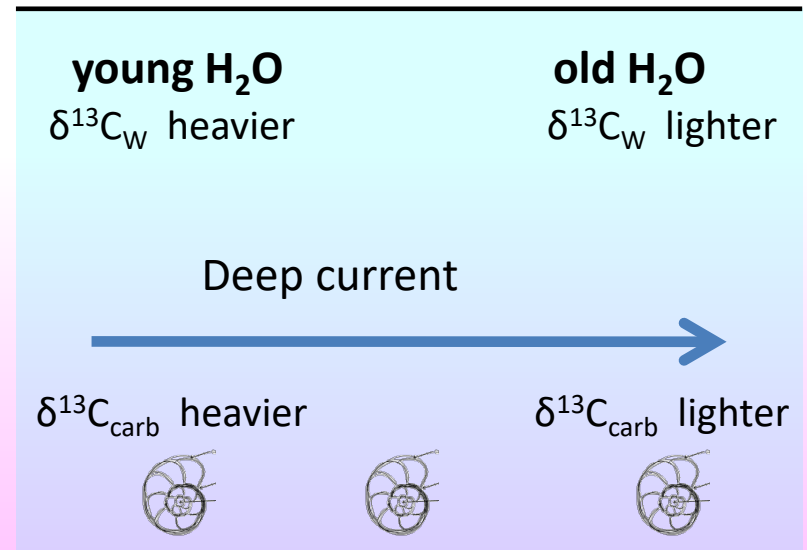
In different oceans, the isotopic composition of benthic (epifaunal) foraminifera having the same age can be used to assess whether the ocean circulation in the past was similar to the present one that involves "OLD"

WATERS IN THE PACIFIC (AVERAGE) AND "YOUNG" WATERS IN THE ATLANTIC.

More generally, with this method we can understand where deep waters (young and isotopically heavy) were formed.

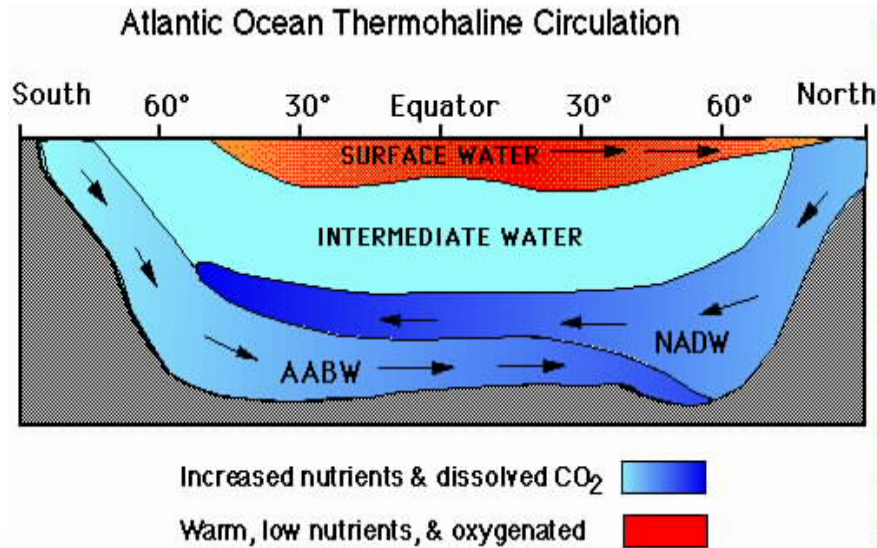
Example:

In the Pleistocene it was seen that the gradients changed between glacial and interglacial



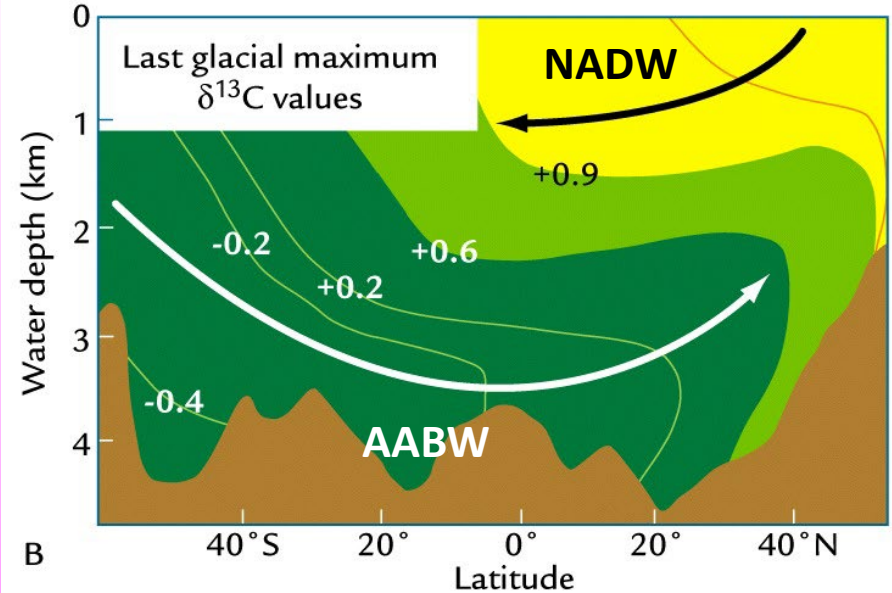
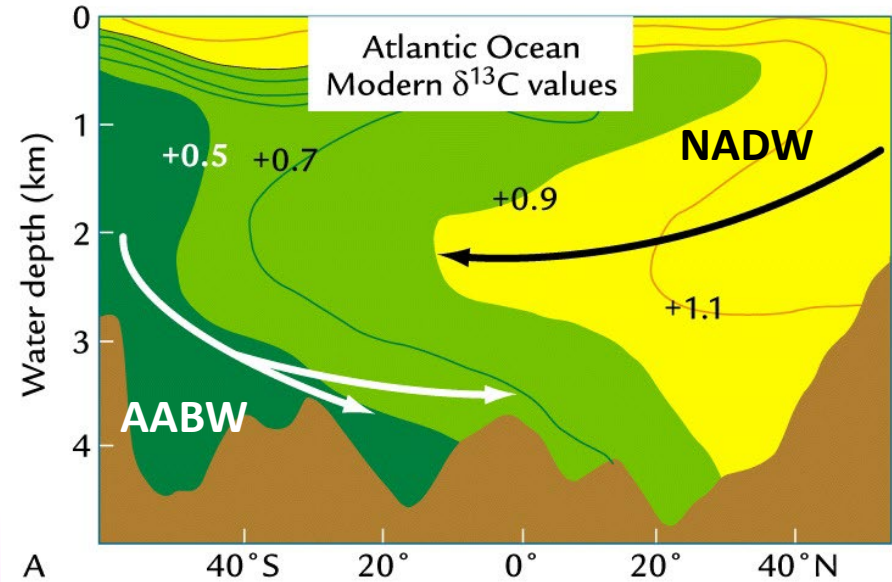
PALEOCEANOGRAPHIC APPLICATIONS - 2

MODERN OCEAN CIRCULATION vs. LGM



The figures on the right show a comparison between the today conditions and the LGM (Last Glacial Maximum) in a portion of the same ocean.

During the LGM, the **NADW** was less extensive, shallower, and less heavy. The bottom of the Atlantic was "invaded" by highly corrosive Antarctic (**AABW**) waters.



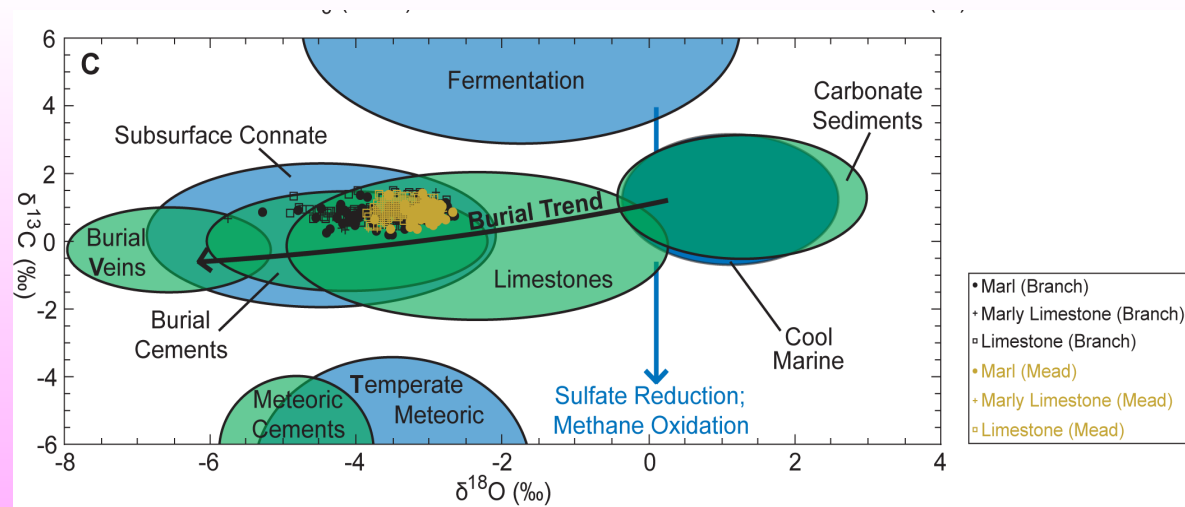
$\delta^{13}\text{C}$ IN THE GEOLOGICAL PAST

One of the most interesting information contained in the C isotopes measured in carbonates is the **variability / changes in $\delta^{13}\text{C}$ of carbonates in the past.**

The most useful information comes from epifaunal benthic foraminifera reflecting the TDIC of the "deep ocean" by far the largest reservoir of C in the Ocean-Atmosphere system. However, total carbonate (bulk) is also used, which often gives similar results.

PRO

The $\delta^{13}\text{C}$ in the carbonates is much less sensitive than the oxygen isotopes to diagenesis, and, therefore, the $\delta^{13}\text{C}$ gives reliable information even in highly lithified rocks, which are the most common.



Note also the significant depletion in ^{18}O relative to typical carbonate in unlithified marine sediment. The stable isotope compositions are consistent with significant local dissolution and reprecipitation of carbonate during burial. Fields of carbonate stable isotope composition are from [Hudson \(1977\)](#) and [Nelson and Campbell \(1996\)](#).

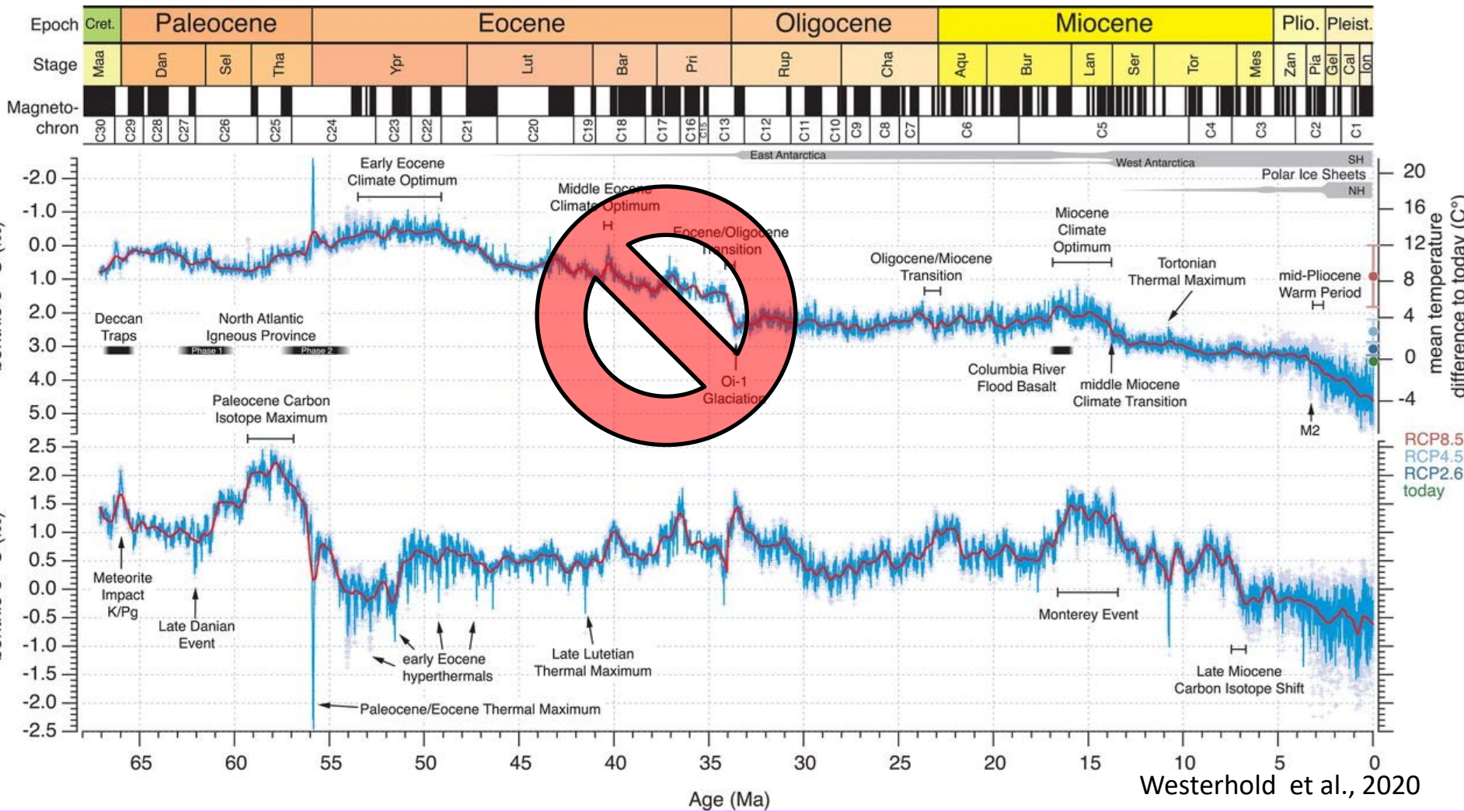
$\delta^{13}\text{C}$ VARIABILITY IN THE GEOLOGICAL PAST

The data collected in the Cenozoic indicate that the values of the $\delta^{13}\text{C}$ of the TDIC of the oceans have changed by varying **at different time scales** and **in different ways**. We recognize:

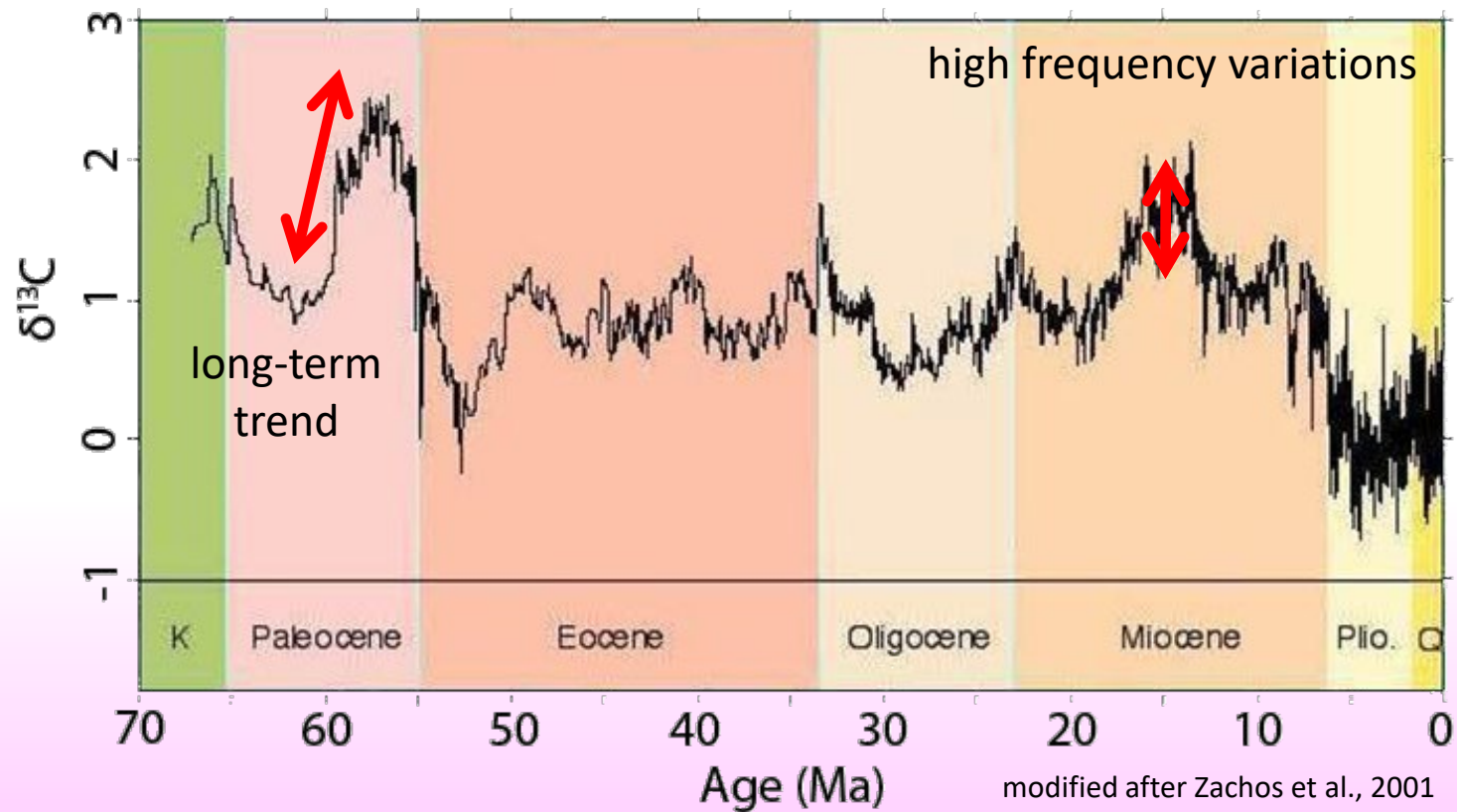
- **Slow and progressive changes in the long geological time;**
- **Cyclical changes on the scale of orbital parameters (e.g., Pleistocene);**
- **Dramatic and very rapid changes, often of short duration, such as those often associated with mass extinctions or climatic variations.**

Let's first look at the type 1 changes and try to understand their causes; we will subsequently deal with cases of type 2) and 3) → e.g., the so-called Paleocene-Eocene Thermal Maximum (PETM).

The causes of gradual changes are presumably different from those of sudden, short-lived changes. We will see...



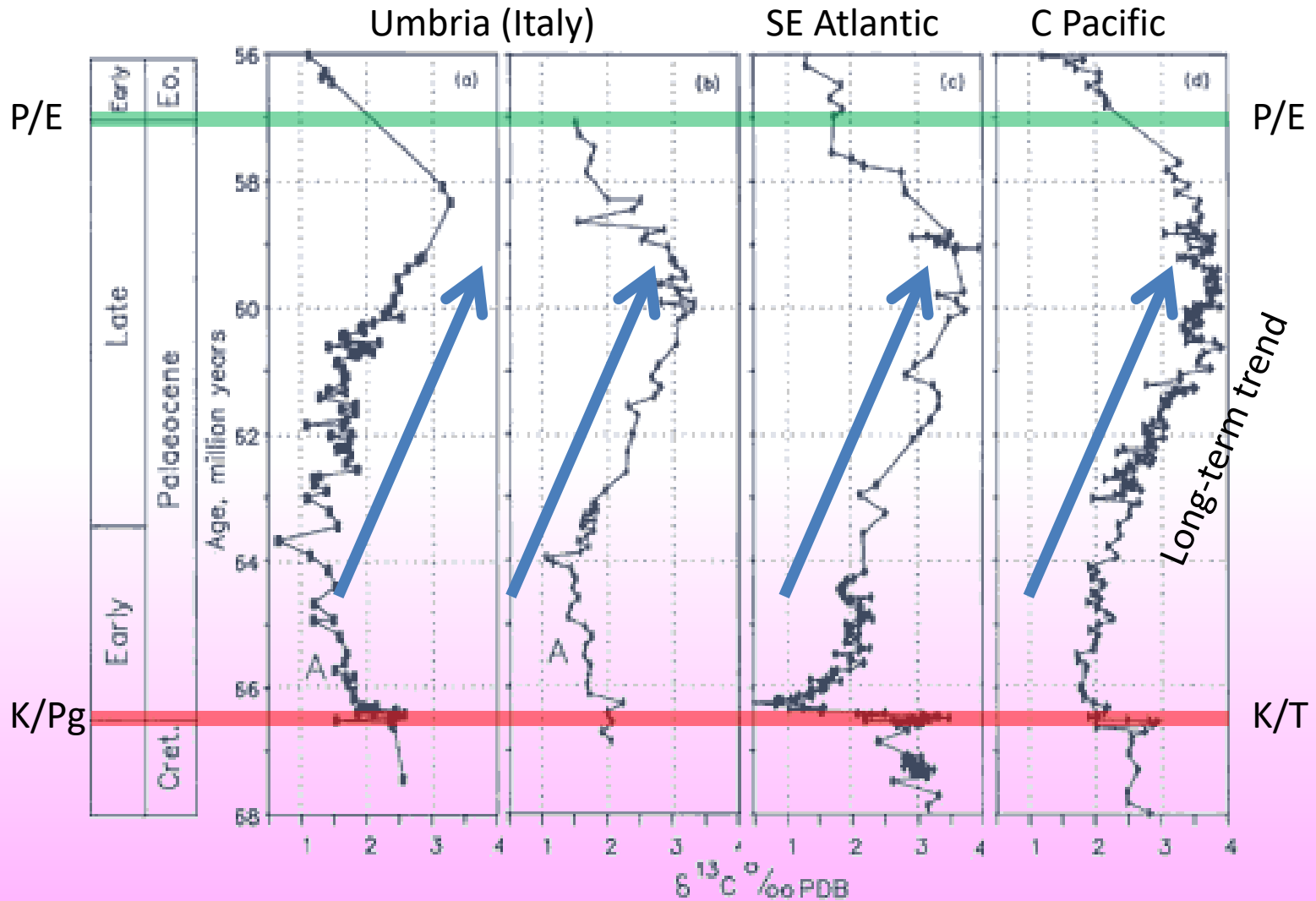
SHORT- AND LONG-TERM VARIATIONS



There are *long-term trends and high frequency variations*.

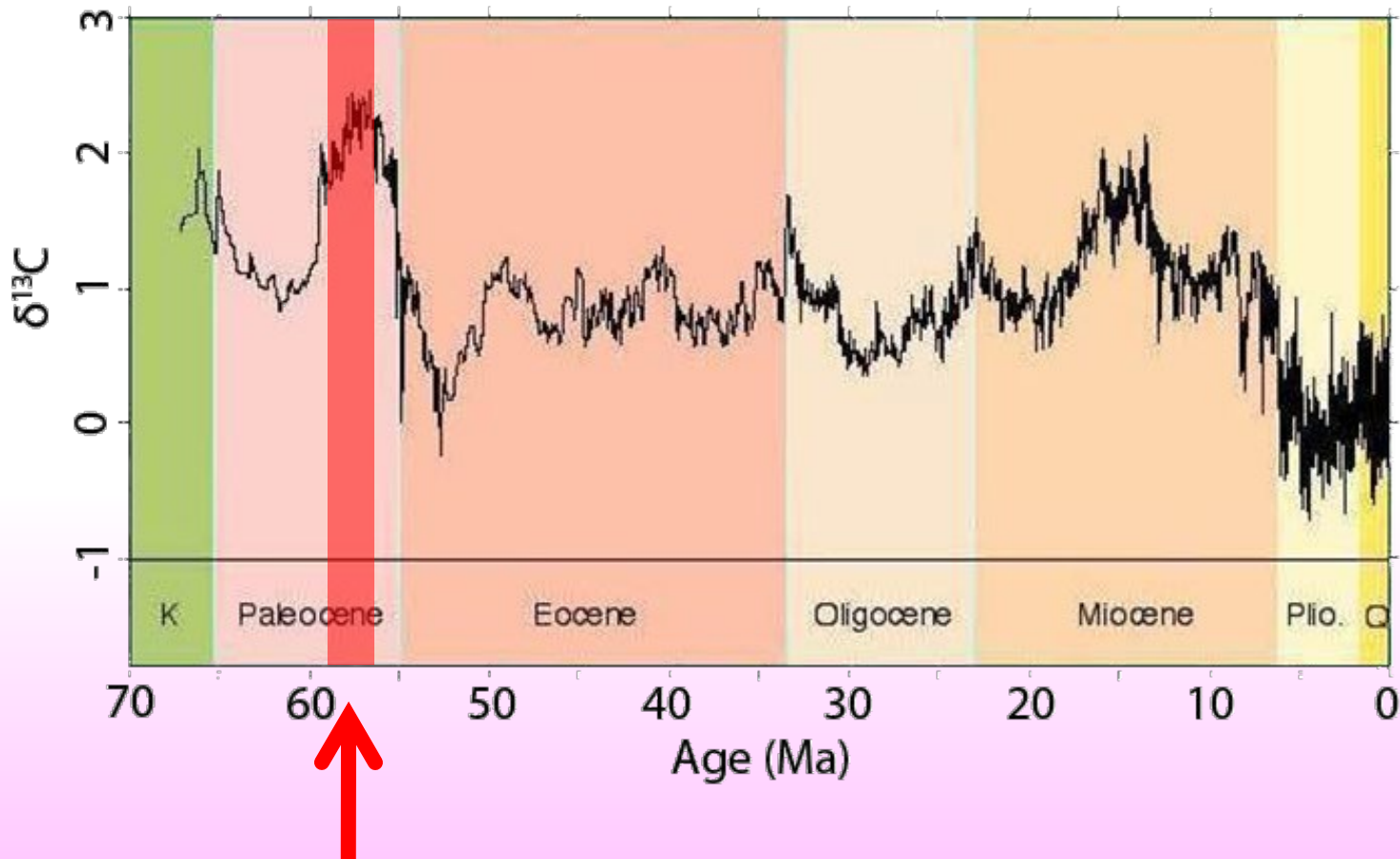
THE CURVE HAS ITS "PERSONALITY", BUT DOES IT HAVE A GLOBAL MEANING?

$\delta^{13}\text{C}_{\text{CARB}}$ DURING THE PALEOCENE



Correlation between Paleocene sequences, from 65 to 55 Ma (between K / Pg and PETM). It starts from low values after the K / Pg and, then, in the upper Paleocene, very high values are reached in all the sequences.

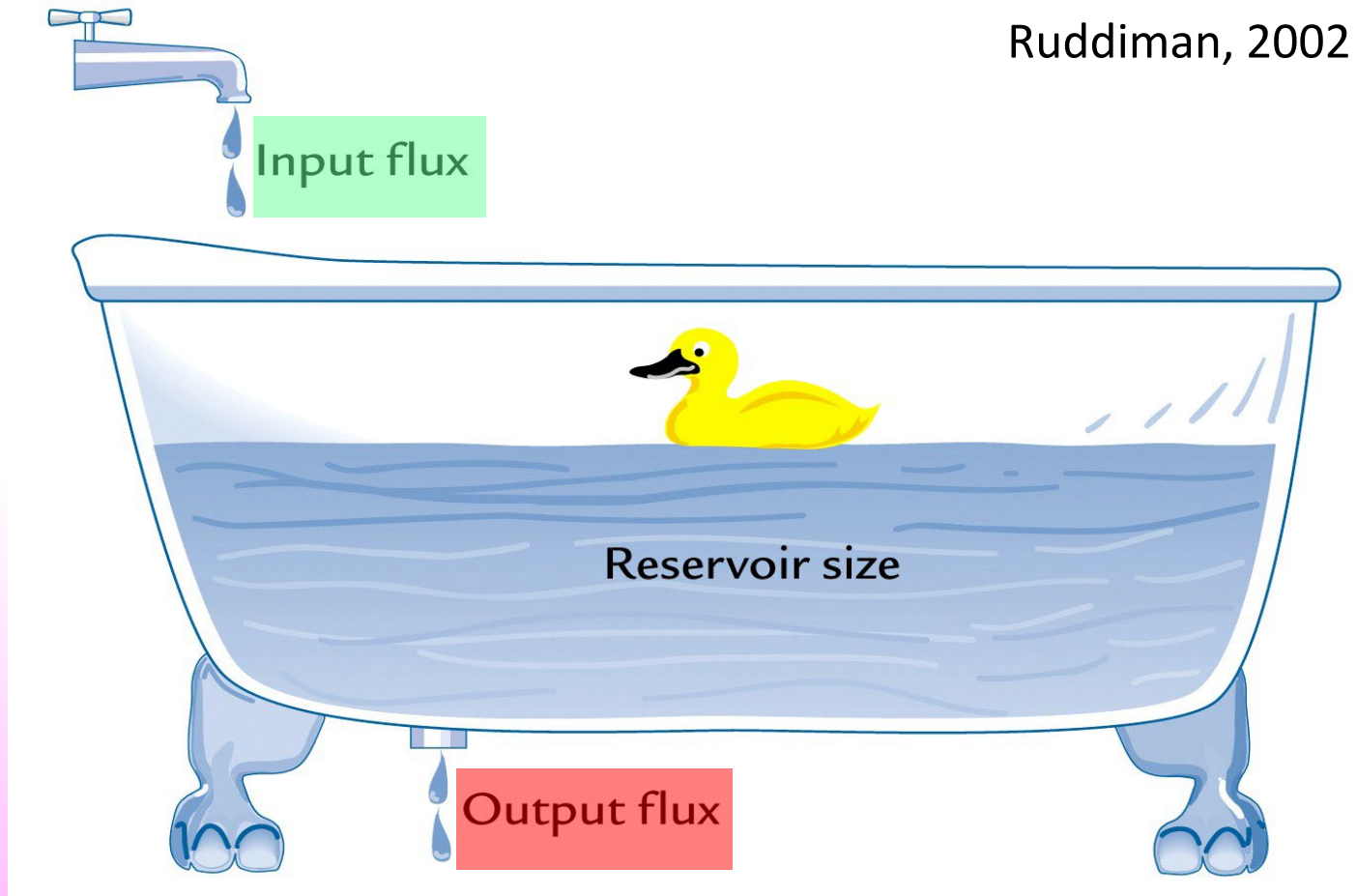
LONG TERM: the *Late Paleocene Carbon Maximum*



The ***Late Paleocene Carbon Maximum*** represents the highest values in $\delta^{13}\text{C}$ of the entire Cenozoic. It is a global character and is therefore an element of stratigraphic correlation, albeit not very precise. Short and sudden events in $\delta^{13}\text{C}$ provide better correlation tools (not very visible in this curve which is very compressed because of the long interval considered - 70 Myr).

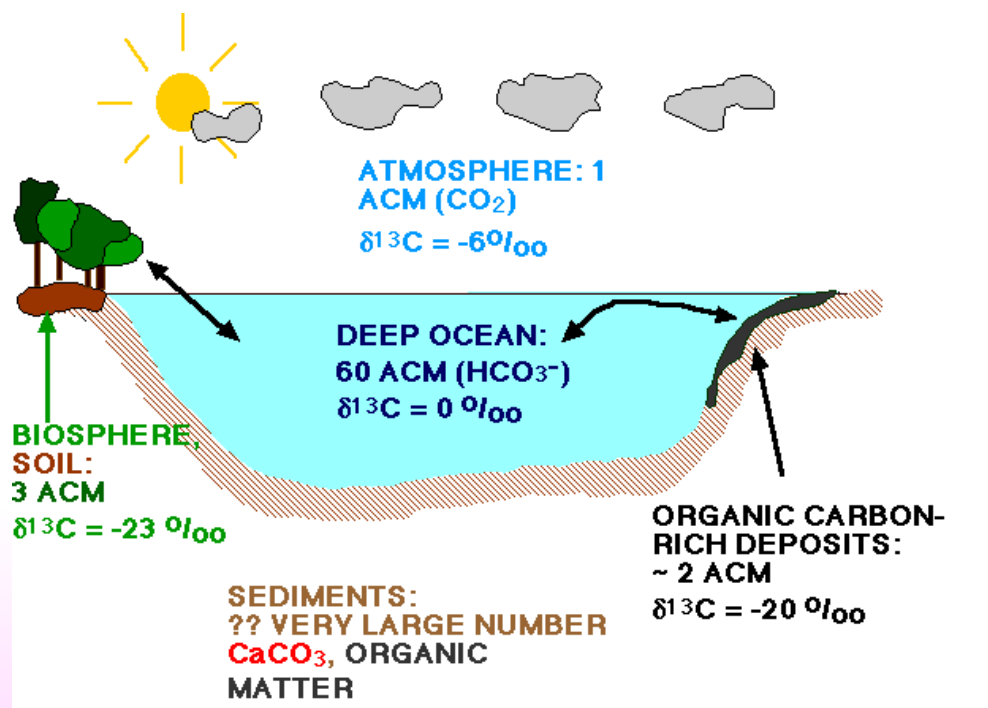
GEOCHEMICAL C RESERVOIRS E FLUXES

Ruddiman, 2002



C reservoirs (like other geochemical reservoirs) are like swimming pools or bathtubs with partially **open taps (input)** and **drain (output) pipes**: The balance between input and output controls the level in the pool and therefore the amount of C in the various reservoirs.

RESERVOIR EXCHANGES



The various reservoirs (*reservoirs*) of carbon on Earth are characterized by having:

- different values of $\delta^{13}\text{C}$,
- different capacity,
- different flow rates (between the various reservoirs).

N.B. Since the mass conservation principle applies, the more ^{12}C is stored in a reservoir, the more the others will change their isotopic composition accordingly.

E.g., if ^{12}C is preferentially stored in organic matter (C_{org} isotopically "light"), the $\delta^{13}\text{C}$ TIDC of the oceans and CO_2 of the atmosphere will become "heavier" (relatively enriched in ^{13}C).

Now, imagine an increase in the organic carbon burial in sediments. In other words, there is a transfer of organic carbon from the ocean to the lithosphere.

What would be the variation in $\delta^{13}\text{C}$ in the ocean due to this exchange?

Exit

Go to **wooclap.com** and use the code **PCCC2023**



Now, imagine an increase in the organic carbon burial in sediments. In other words, there is a transfer of

o

1 The $\delta^{13}\text{C}$ of the ocean increases

2 The $\delta^{13}\text{C}$ of the ocean decrease

3 Nothing happens

0% 0

0% 0

0% 0



<https://app.wooclap.com/events/PCCC2023/0>

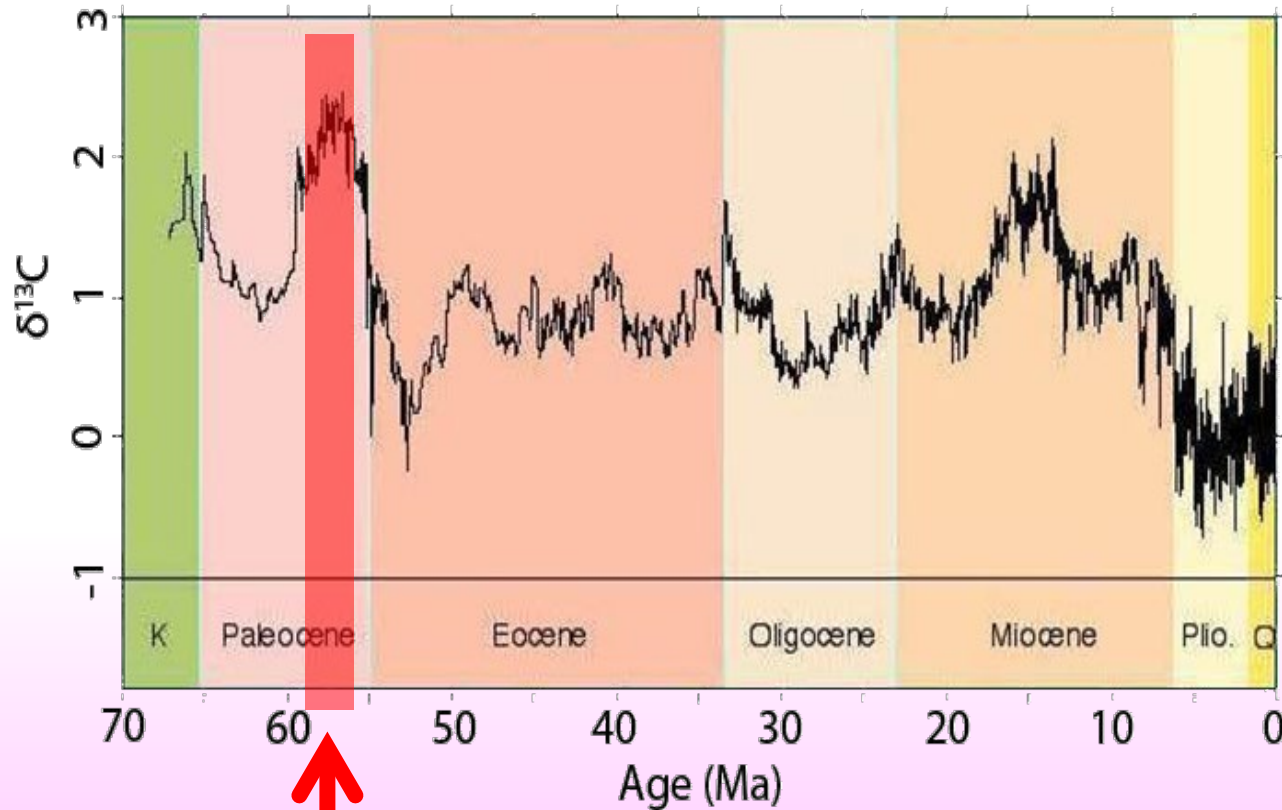
THE $\delta^{13}\text{C}$ IN THE GEOLOGICAL PAST

it is reasonable to assume that if for some reason the fluxes among the various reservoirs change, the values of the $\delta^{13}\text{C}$ of the TDIC of the entire ocean will also change.

- **If we store more organic carbon in sediments** (because biological productivity has increased globally and / or oxygen levels have decreased globally in ocean waters) there will be more ^{12}C removed from the oceans, and hence **the average $\delta^{13}\text{C}$ value of the TDIC of the whole ocean will rise** (e.g., Late Paleocene Carbon Maximum, Blake shale).
- **If we imagine large quantities of organic matter (for example fossil coal) are being eroded from the land** (for example in the formation of mountain chains), then the **average value of the $\delta^{13}\text{C}$ of the TDIC of the oceans will decrease**. Note that, in this case, the CO_2 of the atmosphere will also increase → *whatever happens to the isotopic composition of the oceans is transferred to the atmosphere.*

These mechanisms may explain the slow changes in carbonate $\delta^{13}\text{C}$ which, presumably, will therefore be global.

CAUSES of LONG-TERM $\delta^{13}\text{C}$ IN THE GEOLOGICAL PAST

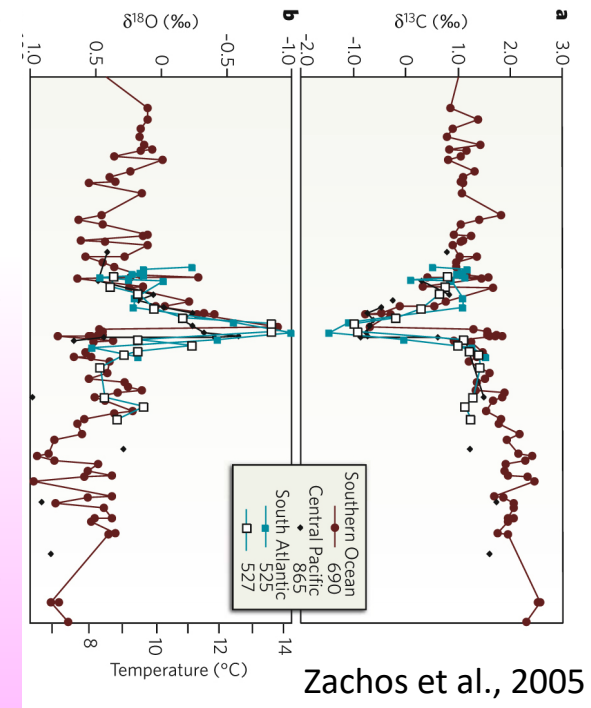
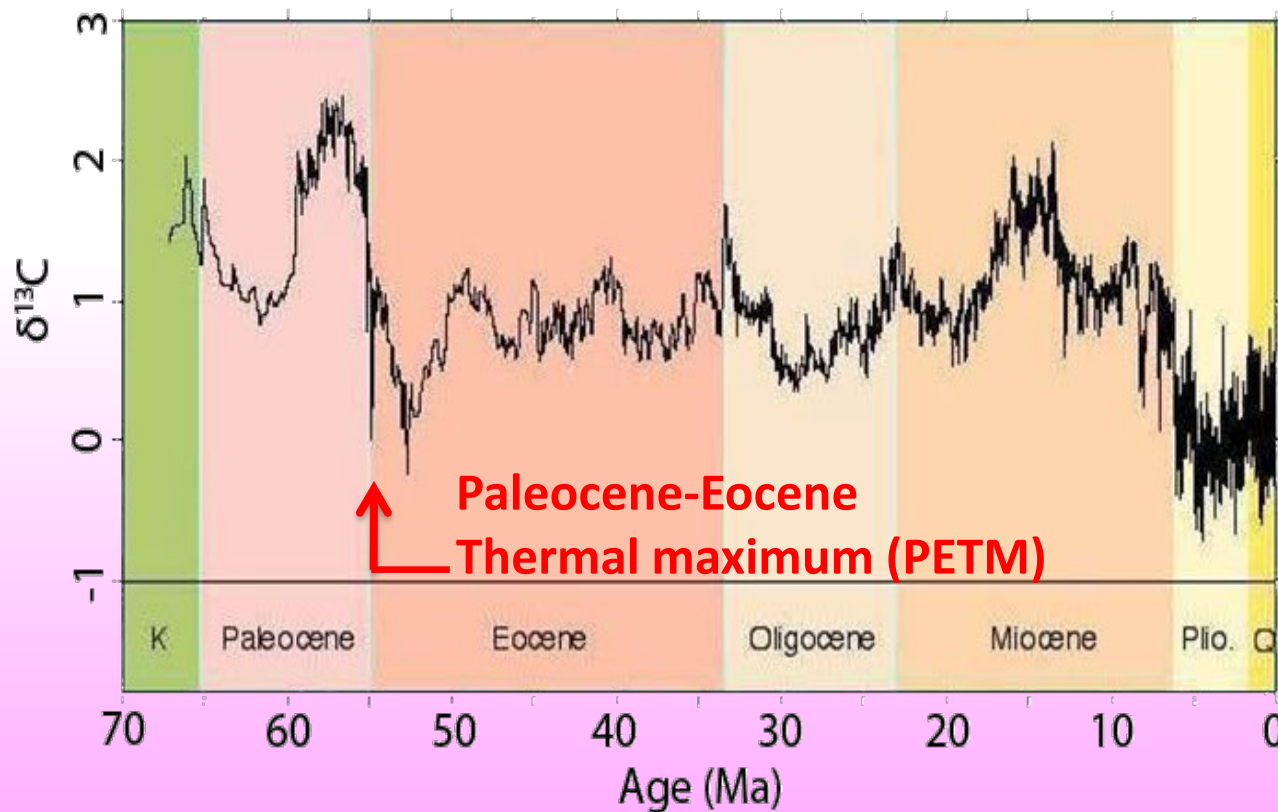


Widely shared opinion to explain the variations in the isotope composition of carbon:

positive shifts can be caused by a removal of organic matter (^{13}C -enriched sea water), while **negative excursions** can be explained by the introduction of light (^{13}C -depleted) CO_2 or HCO_3^- of volcanic and detrital origin or from "light" reservoirs .

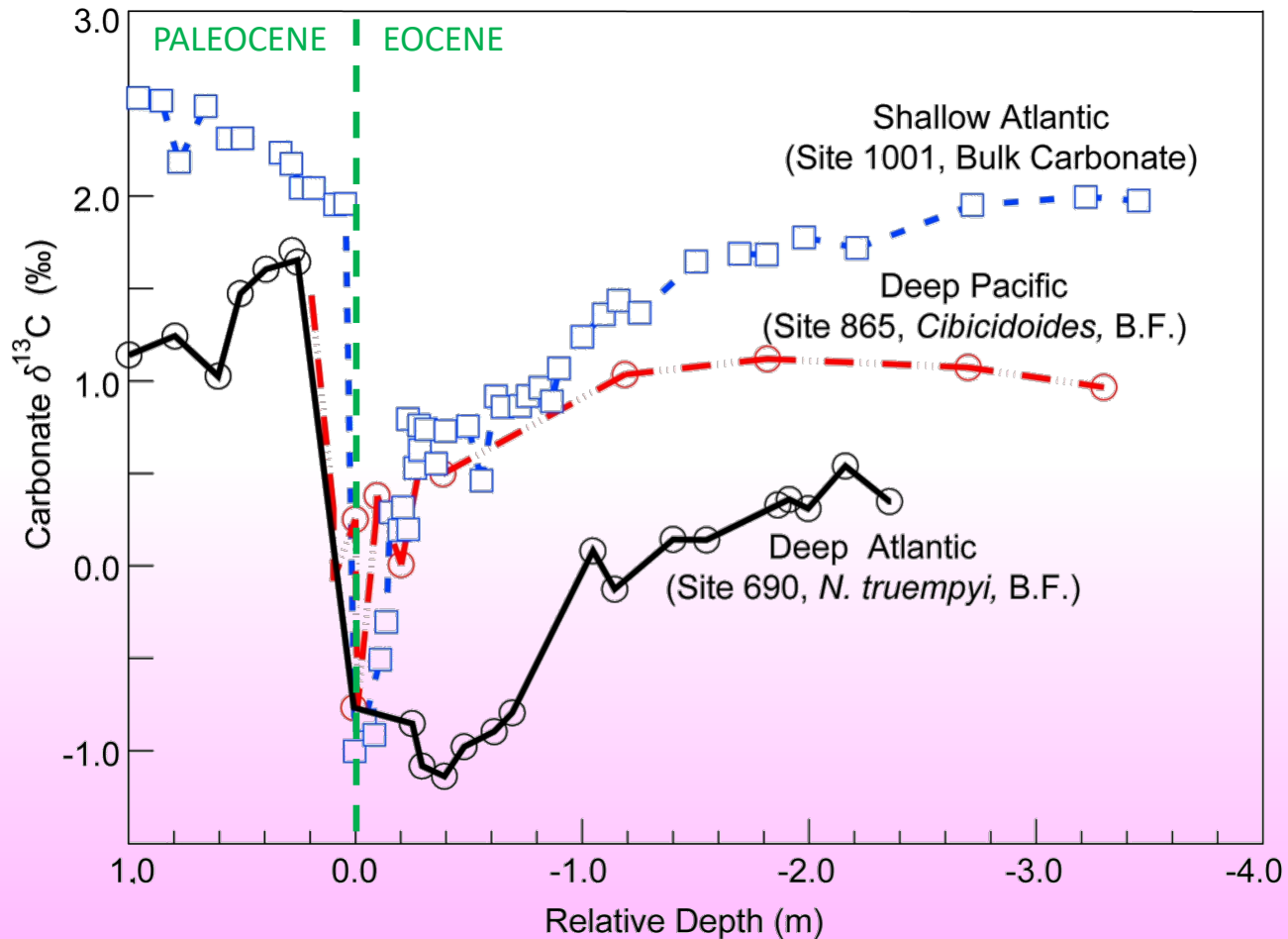
EXAMPLE OF DRAMATIC, SUDDEN AND TRANSIENT VARIABILITY OF $\delta^{13}\text{C}$: THE PETM

Note the prominent and short-lasting negative excursion at the P / E boundary. Simultaneous to the negative shift of $\delta^{13}\text{C}$ there is a significant and global lightening of $\delta^{18}\text{O}$ in foraminifera \rightarrow warming of 5-8



The PETM is poorly visible in this low resolution curve, it remains compressed for graphic reasons. If we go into detail

PALEOCENE/EOCENE THERMAL MAXIMUM: $\delta^{13}\text{C}$



High resolution documentation of carbon isotopes from 3 ODP sites located in different geographic areas. Data have a common scale of depths, where the minimum of $\delta^{13}\text{C}$ is set at 0.0 m. Benthic foraminifera at Site 690, Maud Rise, South Atlantic (Kennett and Stott, 1991). Benthic foraminifera at Site 865, Allison Guyot, Equatorial Pacific (Bralower et al., 1995). Bulk carbonate at Site 1001, Nicaraguan Rise, Caribbean (Bralower et al., 1997). In this figure, “deep” refers to intermediate depths, 1500-2000 m.

Note the sudden decrease in $\delta^{13}\text{C}$ of -2.5 to -3 ‰ in ca. 5-20 cm followed by a return to the initial values in 1-4 m.

PETM

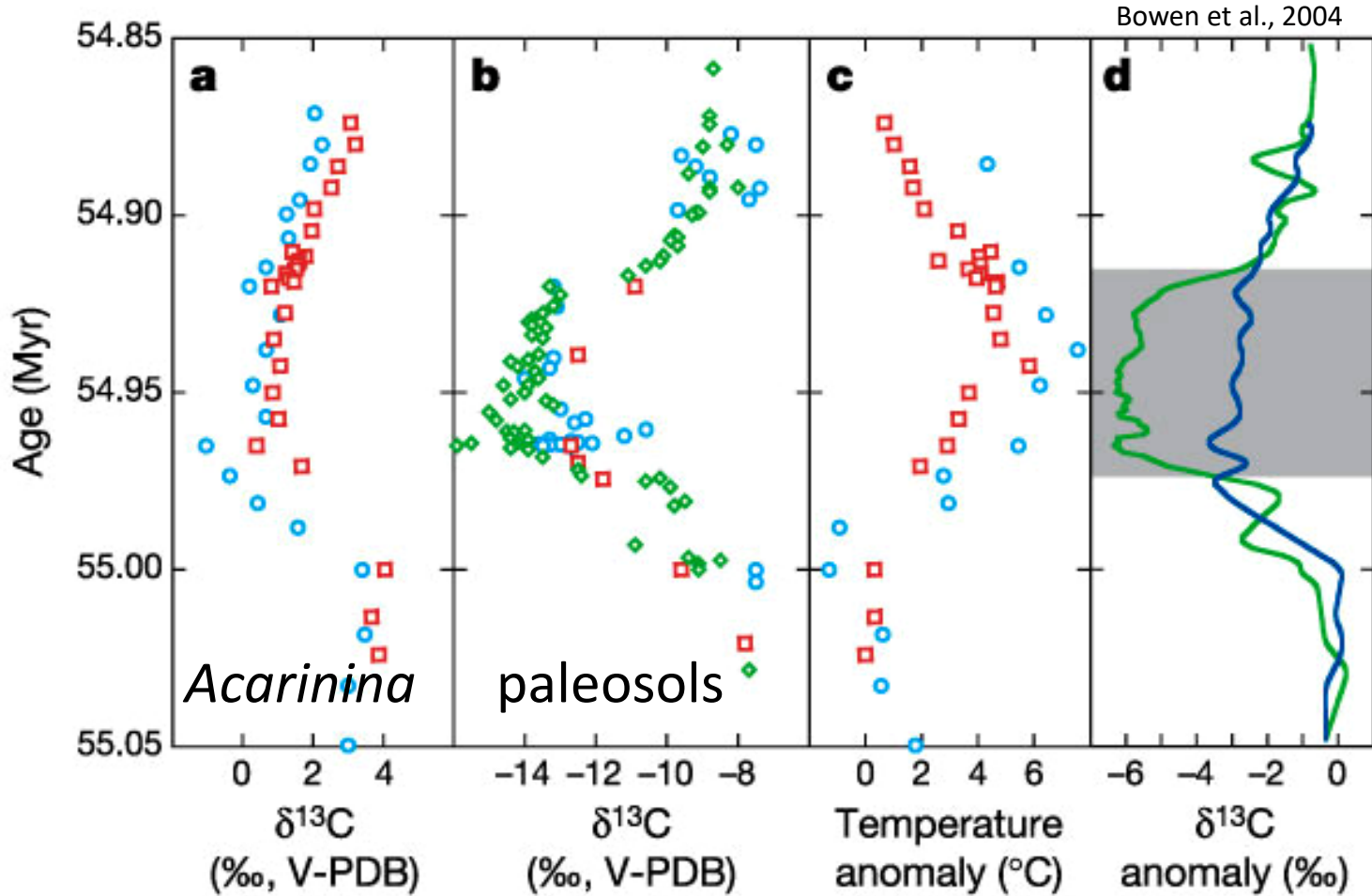
What is PETM from an isotopic point of view?

The PETM represents a ^{12}C injection into the ocean-atmosphere system.

**Carbon
isotope
Excursion**

2–3 ‰
marine

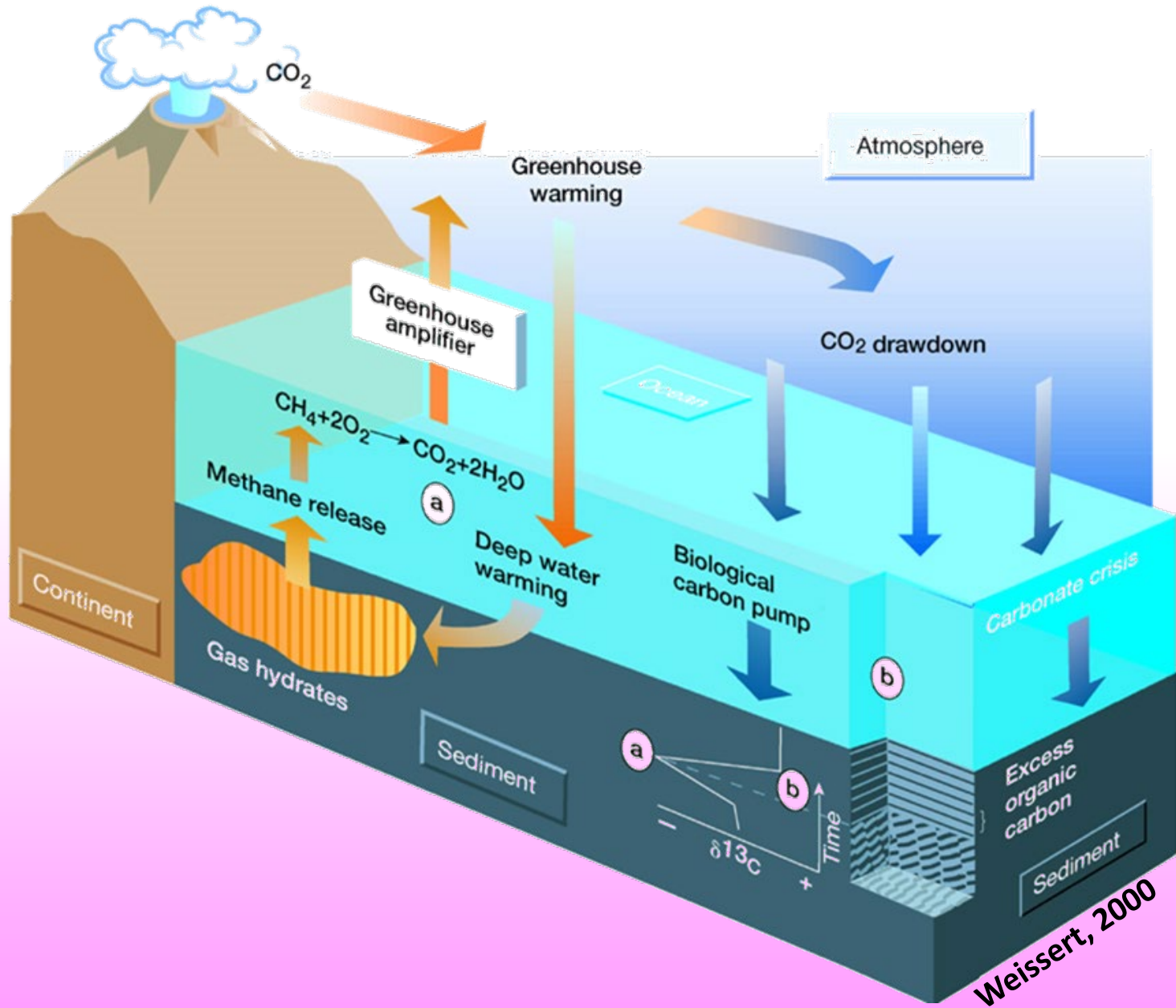
5–6 ‰
continental



...unknown **SOURCE** and **TRIGGER** of the **PETM**

- ☞ **Methane release** ($\delta^{13}\text{C} = -60\text{‰}$)
(Dickens et al., 1995)
- ☞ **Peat of organic carbon** ($\delta^{13}\text{C} = -30\text{‰}$)
(Kurtz et al., 2003)
- ☞ **Thermogenic Carbon** ($\delta^{13}\text{C} = -35/-50 \text{‰}$)
(Svensen et al., 2004)
- ☞ **Volcanic CO₂** ($\delta^{13}\text{C} = -6\text{‰}$)
(Schimtz al., 1997)
- ☞ **Comet impact** ($\delta^{13}\text{C} = -45\text{‰}$)
(Kent et al., 2003)

...unknown source and trigger of the PETM



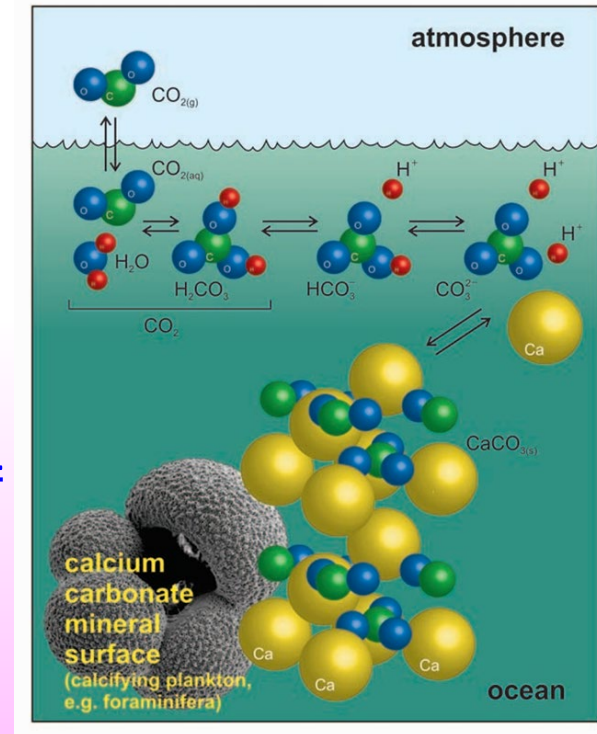
GLOBAL ENVIRONMENTAL AND BIOTIC PERTURBATIONS

HUGE CHANGES IN THE CHEMISTRY OF THE OCEANS INCLUDING:

- 👉 5-8 °C rise in global temperature
- 👉 A major acidification event
- 👉 Strong dissolution of seafloor carbonate
- 👉 > sea level (thermal expansion) + circulation overturning

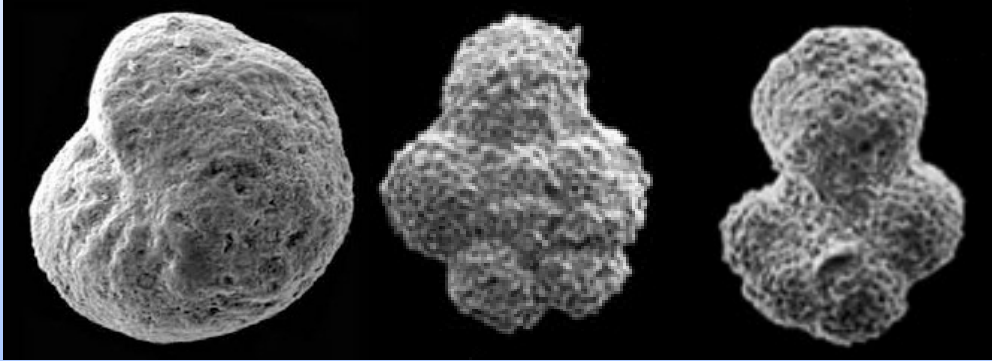
HUGE CHANGES IN MARINE AND TERRESTRIAL BIOTA INCLUDING:

- ✓ Mass extinction of deep-water benthic foraminifera (BEE)
- ✓ Radiation of new orders of mammals (MDE)
- ✓ Transient proliferation of short-lived unusual plankton (PFET – CNET – *A. augustum* Acme)



Changes in marine biota

Benthic & Planktonic Foraminifera



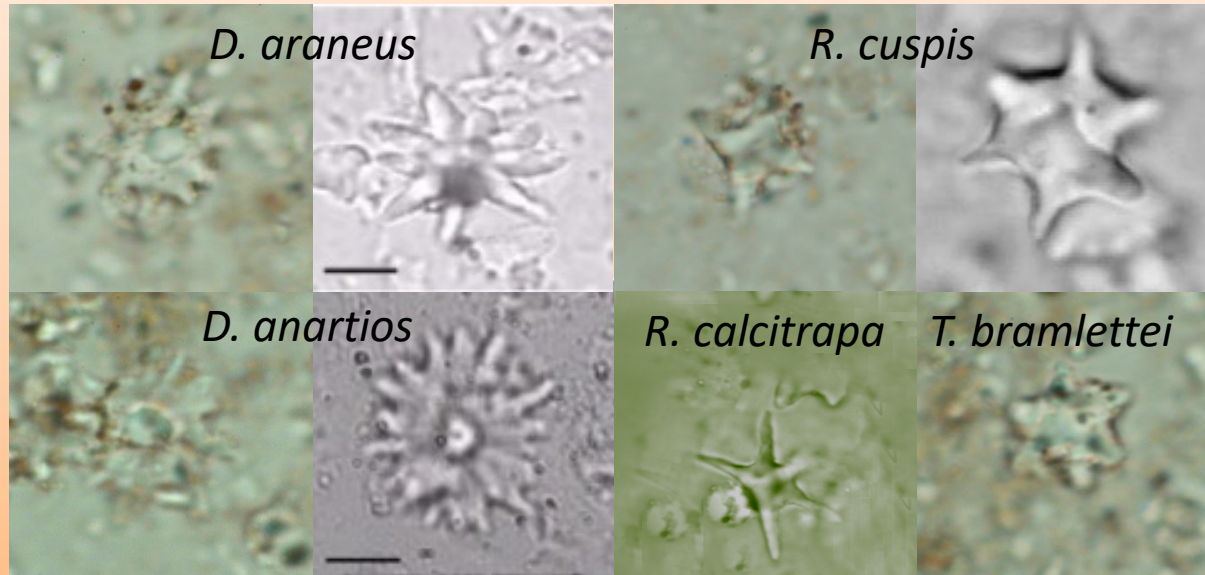
G. beccariiformis *A. sibaiyaensis* *A. africana*

Dinoflagellates



Apectodinium augustum

Calcareous nannofossils



D. araneus

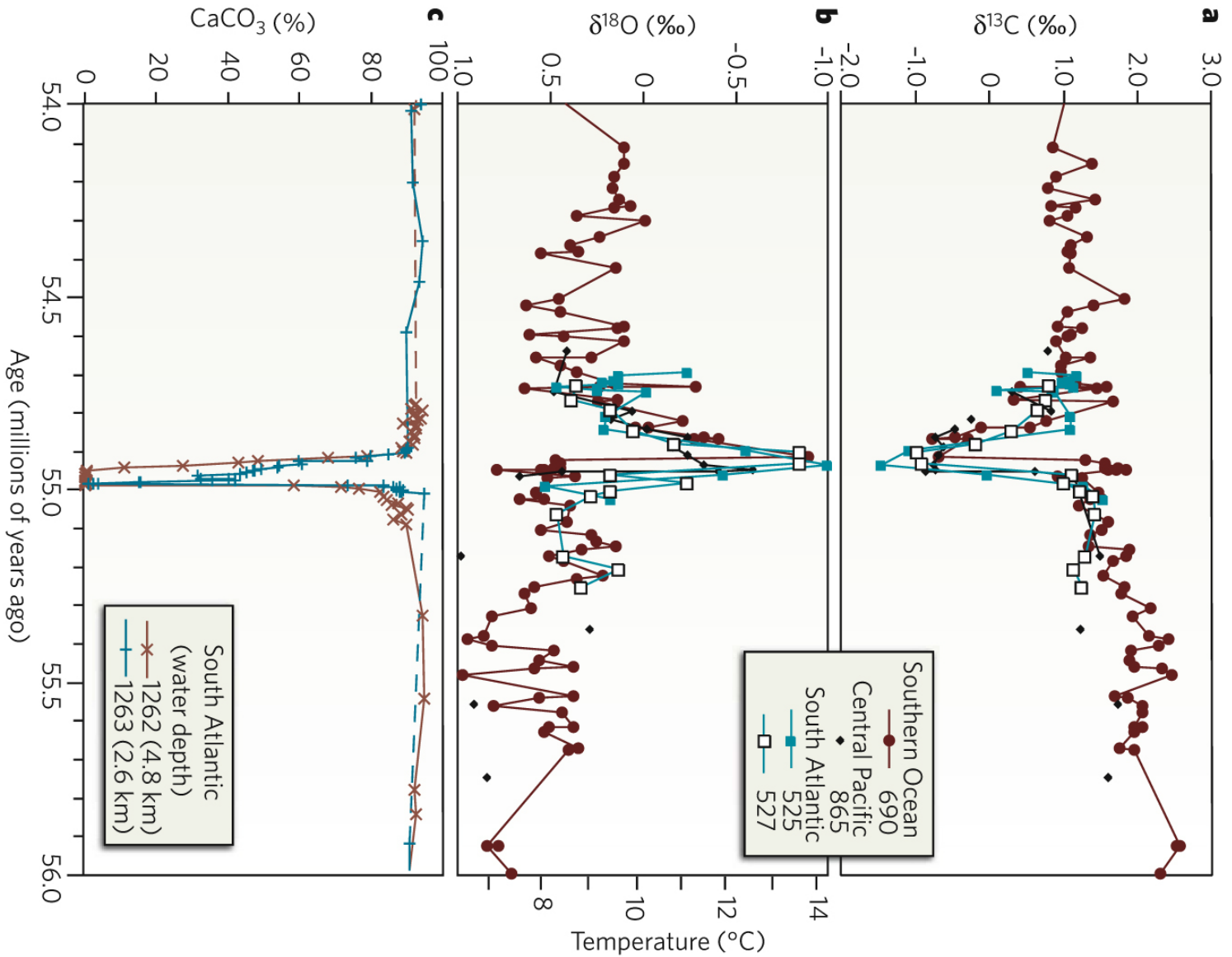
R. cuspis

D. anartios

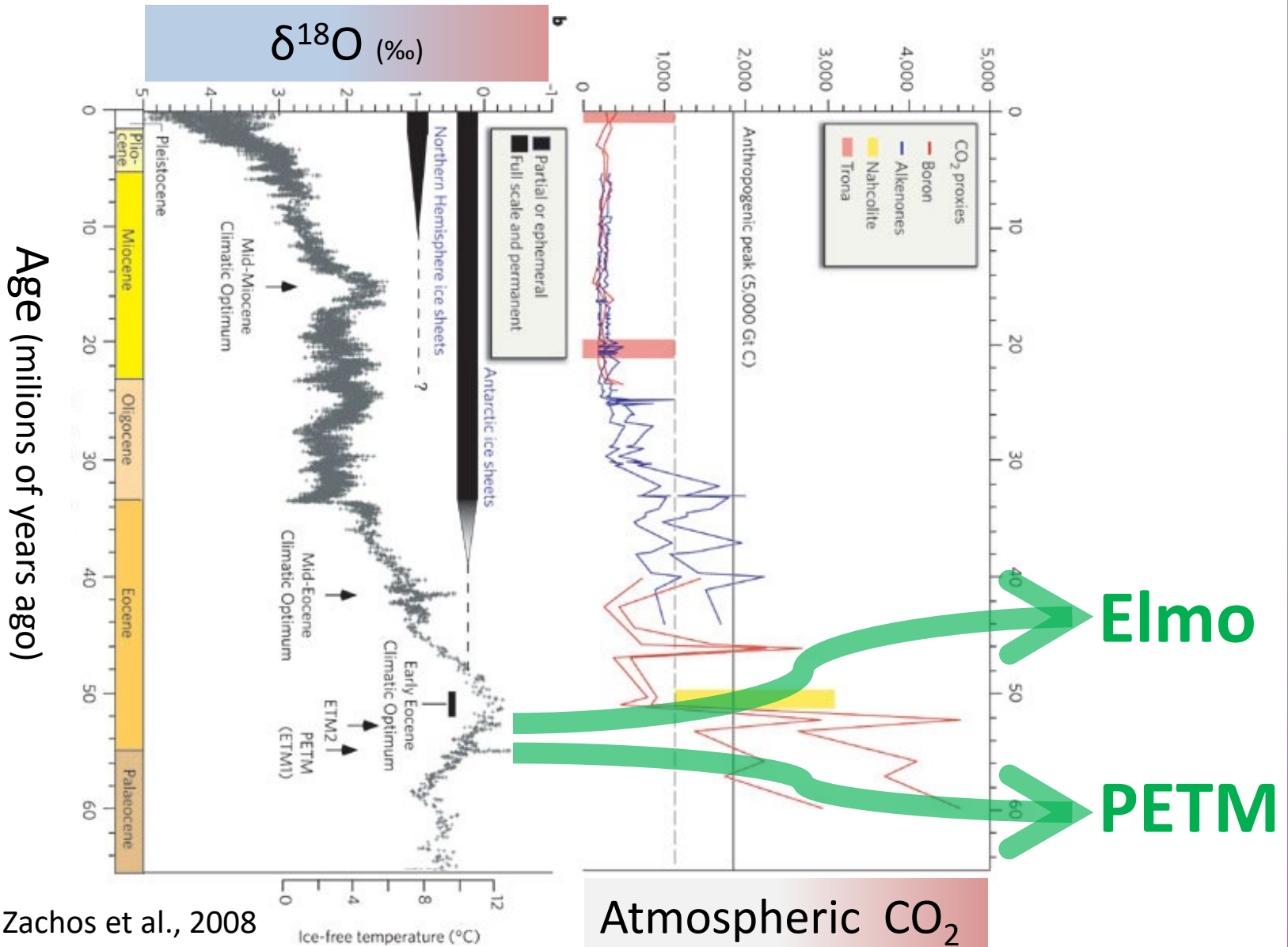
R. calcitrapa

T. bramlettei

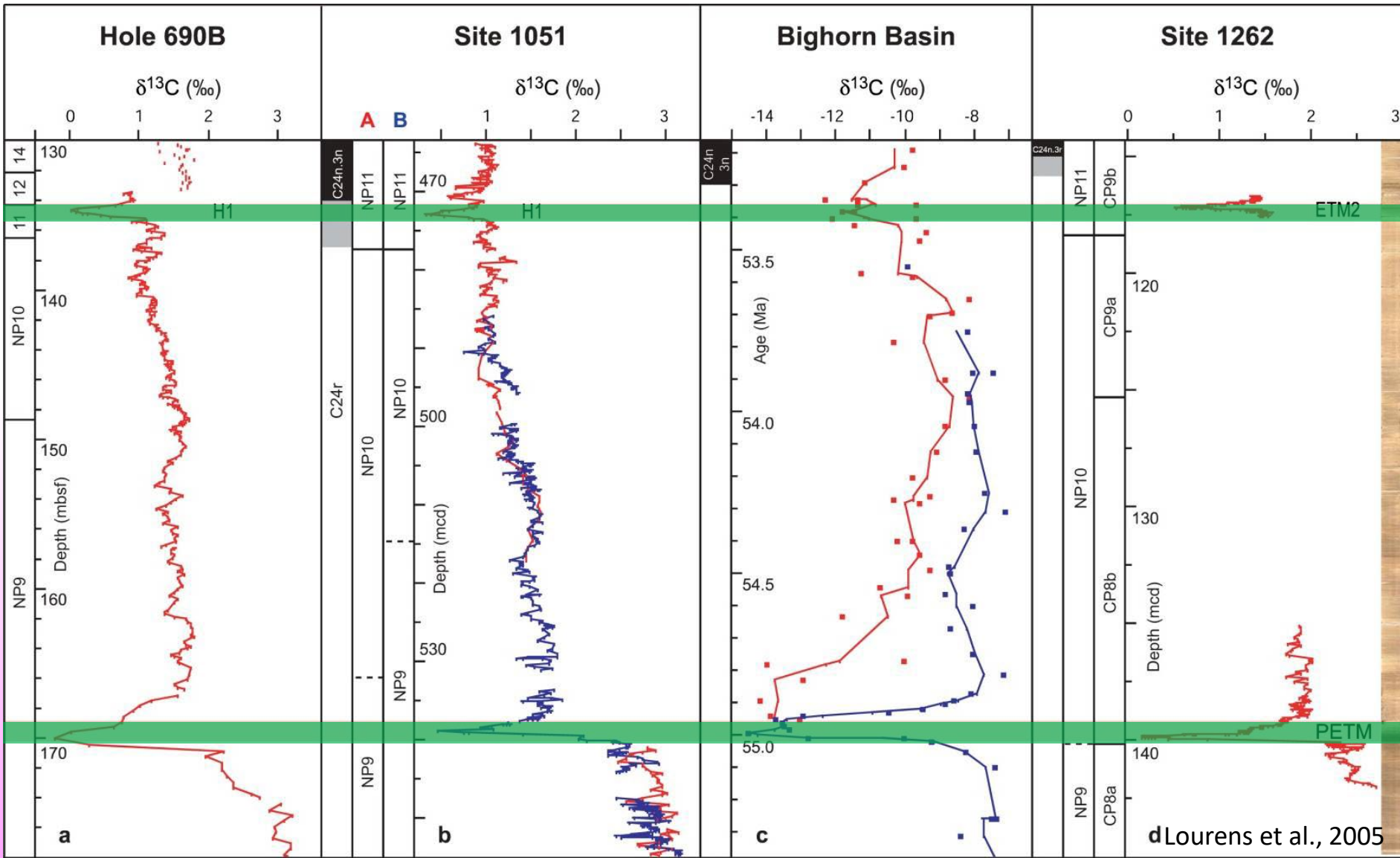
PALEOCENE EOCENE THERMAL MAXIMUM



Early Eocene climatic regime

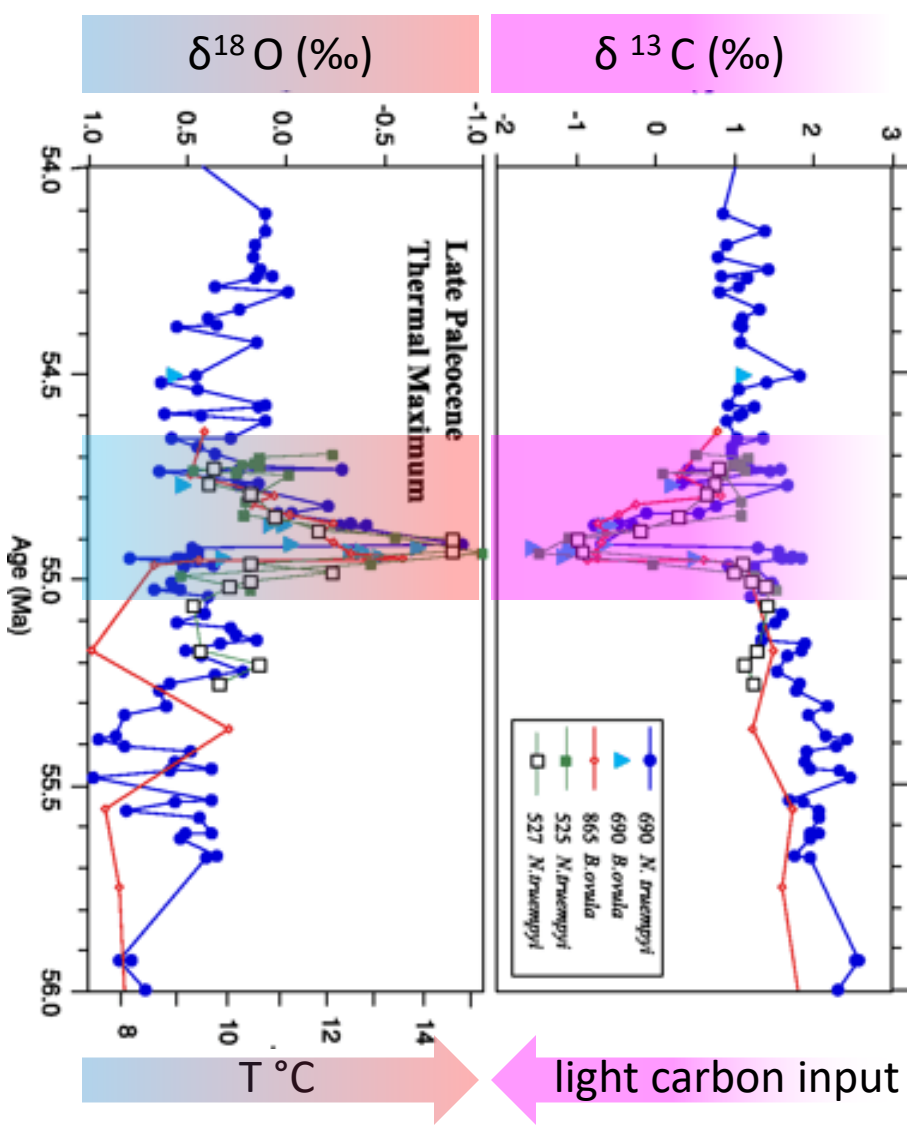


PETM (ETM1) e ELMO (ETM2, H1)



Escursioni negative di $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ ma anche....

WHAT HAPPENED DURING THE PETM?



Zachos et al., 2001

$T > 5-8^\circ\text{C}$

Light carbon input:
negative CIE $\delta^{13}\text{C}$ (‰)

What happens when carbon is rapidly injected into the ocean-atmosphere system?

CH_4 (e.g.) + $2\text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
oxidation in the atmosphere- $p\text{CO}_2 >$

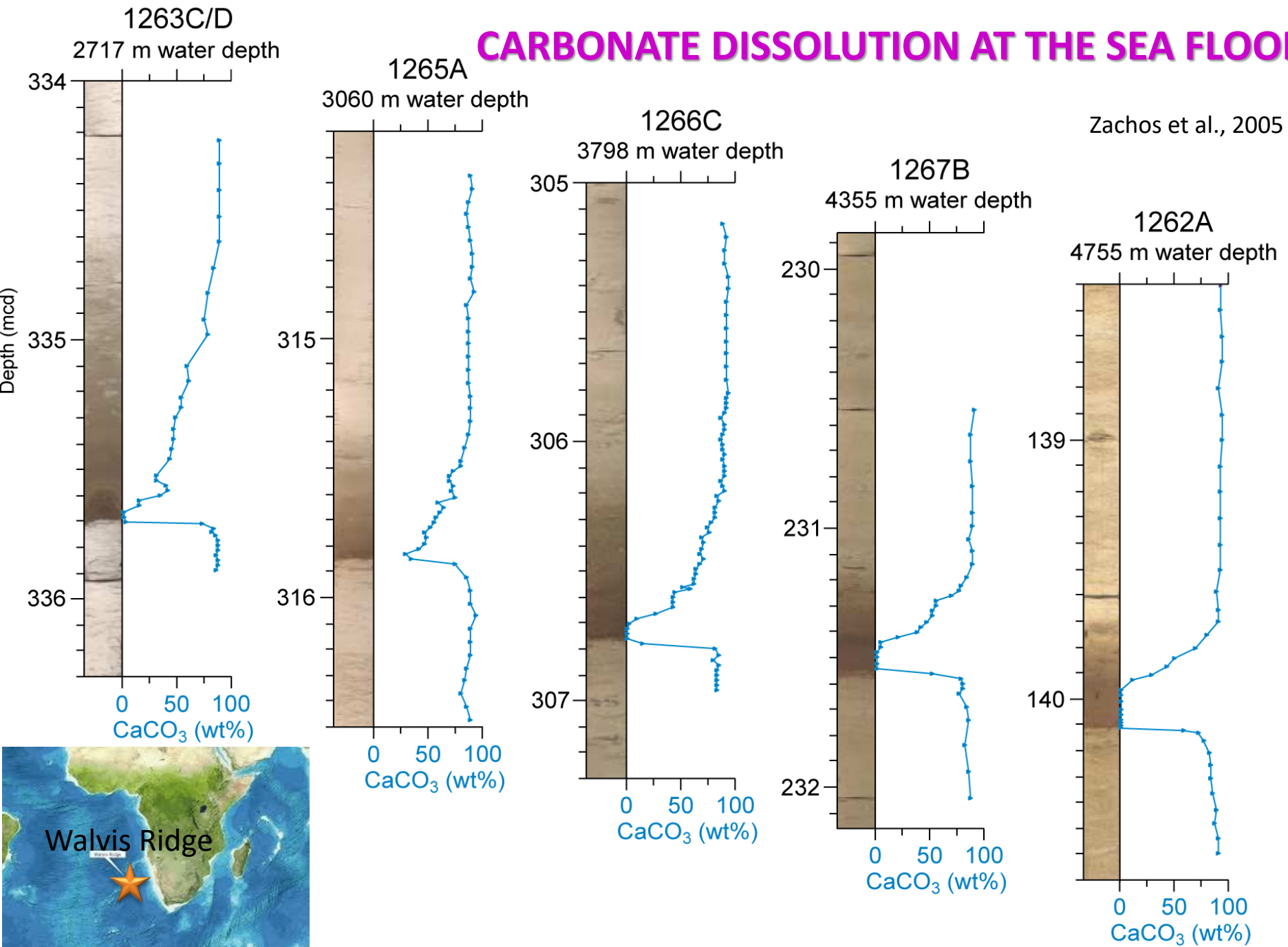
$\text{CO}_2 + \text{H}_2\text{O} + \text{CO}_3^{2-} \leftrightarrow 2\text{HCO}_3^-$
 $\text{CO}_3^{2-} < - \text{pH} <$



dissolution of the carbonates at the bottom \rightarrow CCD rise

CARBONATE DISSOLUTION AT THE SEA FLOOR

Zachos et al., 2005

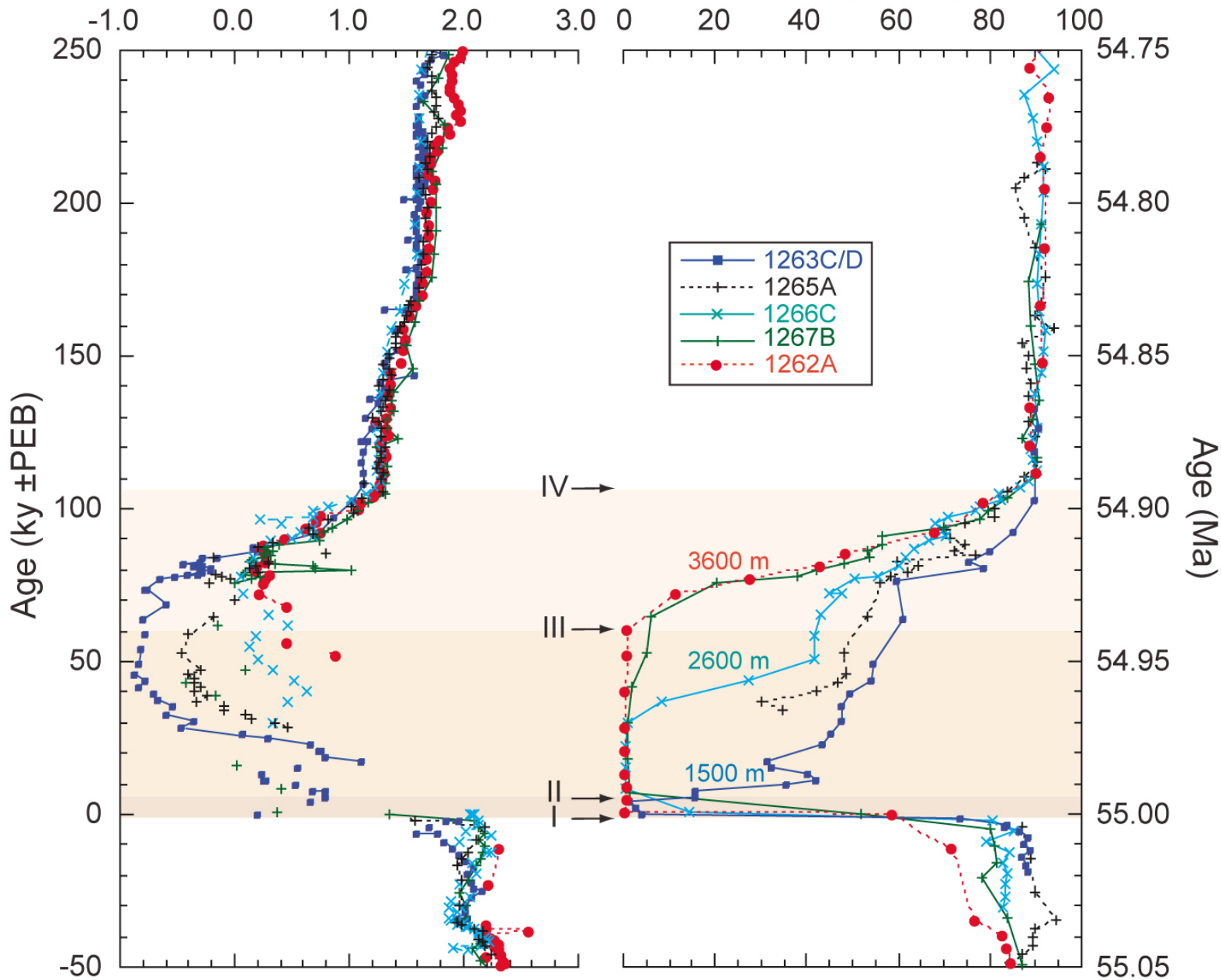


Zachos et al., 2005

$\delta^{13}\text{C}$ (vPDB)

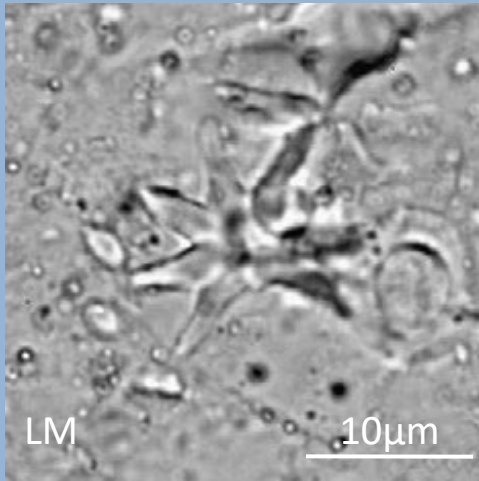
CaCO_3 (wt%)

CCD SHALLOWING

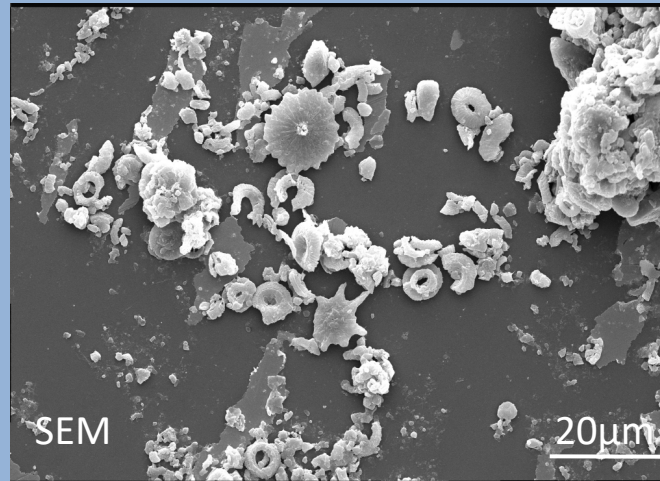


ODP Site 1262 - PETM

D. araneus

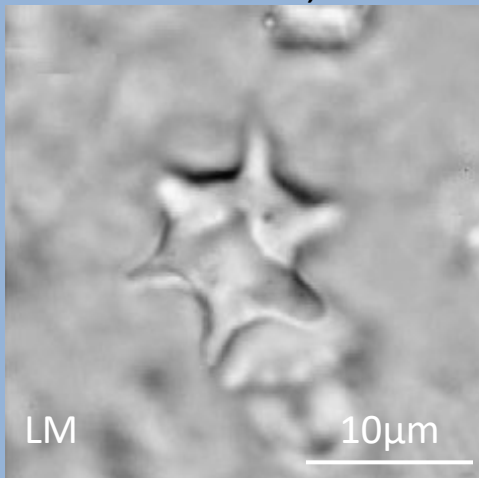


1262B-15H-3, 49cm

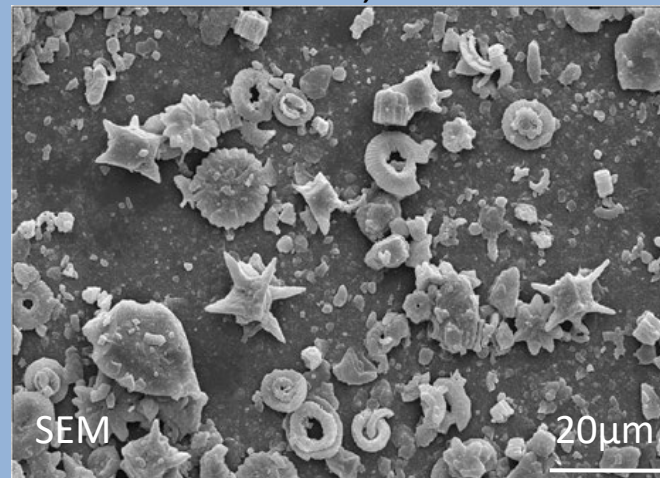


1262B-15H-3, 48-49 cm

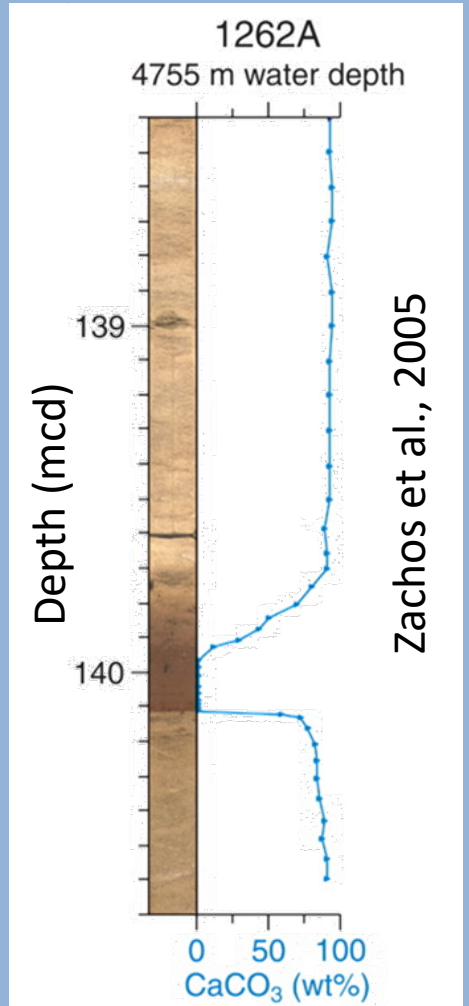
Rhomboaster



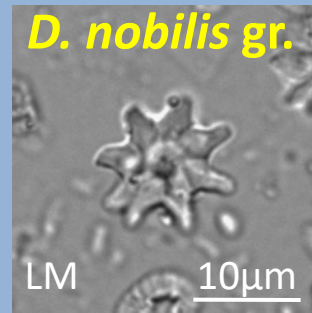
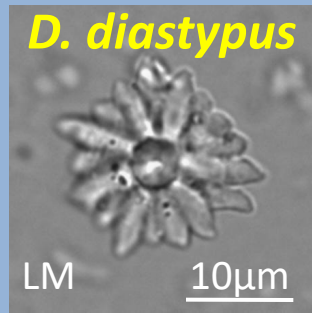
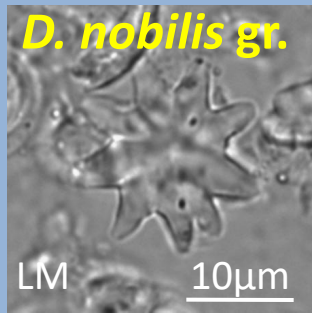
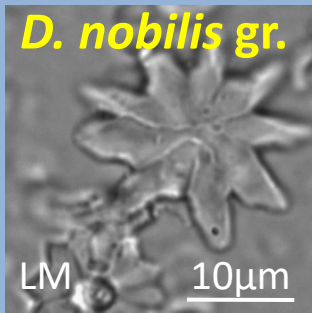
1262B-15H-3, 49cm



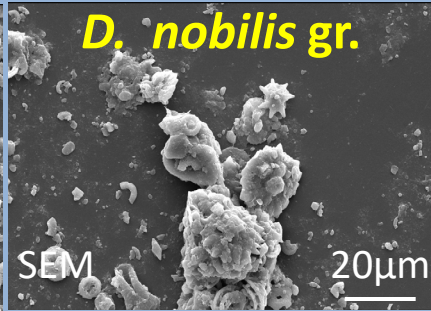
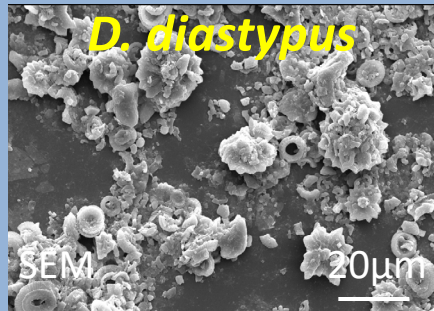
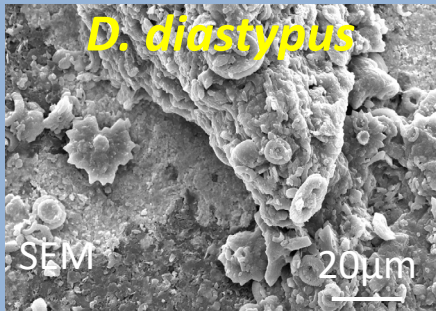
1262B-15H-3, 48-49 cm.



ODP Site 1262 - Elmo



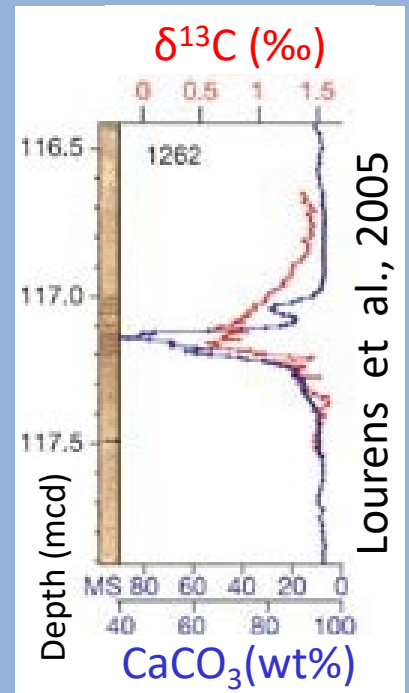
1262A 11H-5, 8.5-9cm 1262A 11H-5, 8.5-9cm 1262A 11H-5, 8.5-9cm 1262A 11H-5, 8.5-9cm



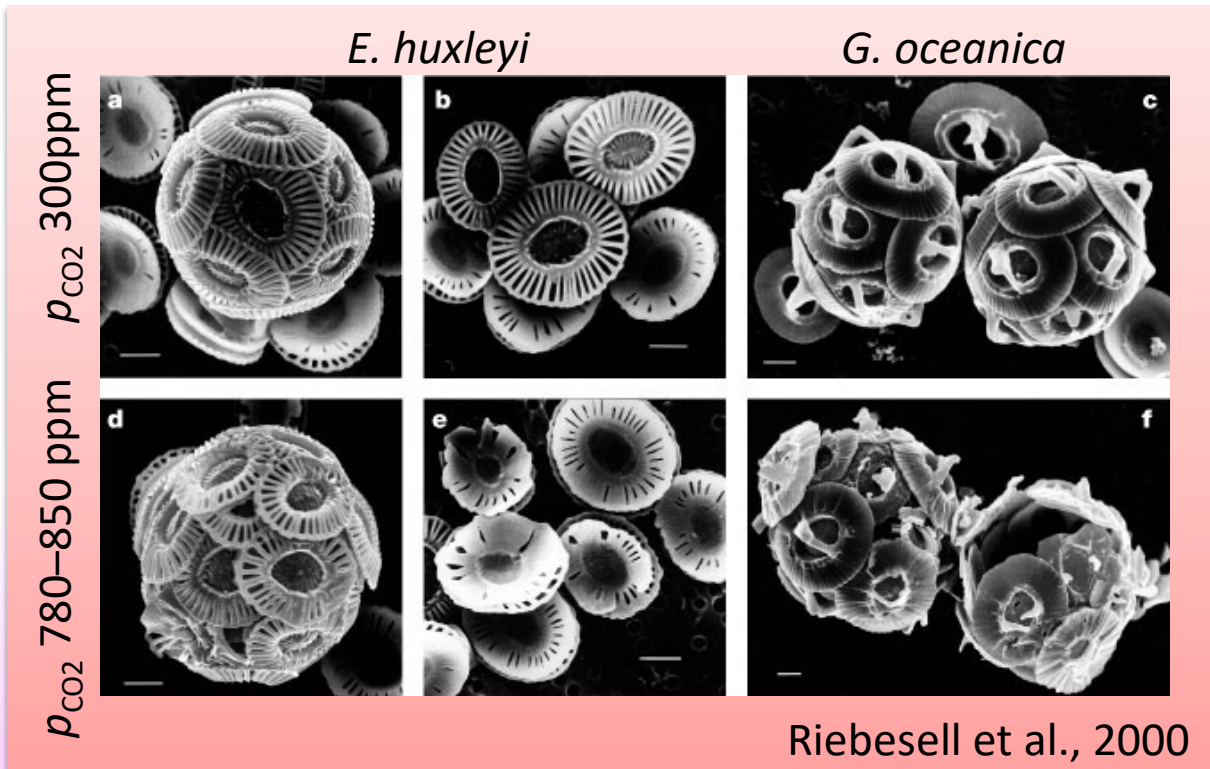
1262A 11H-5, 8.5-9cm

1262A 11H-5, 8-8.5cm

1262A 11H-5, 9-9.5cm



PALEOANALOGUES?



MALFORMATIONS
IN VITRO CULTURE



CO_3^{2-} decrease
pH decrease

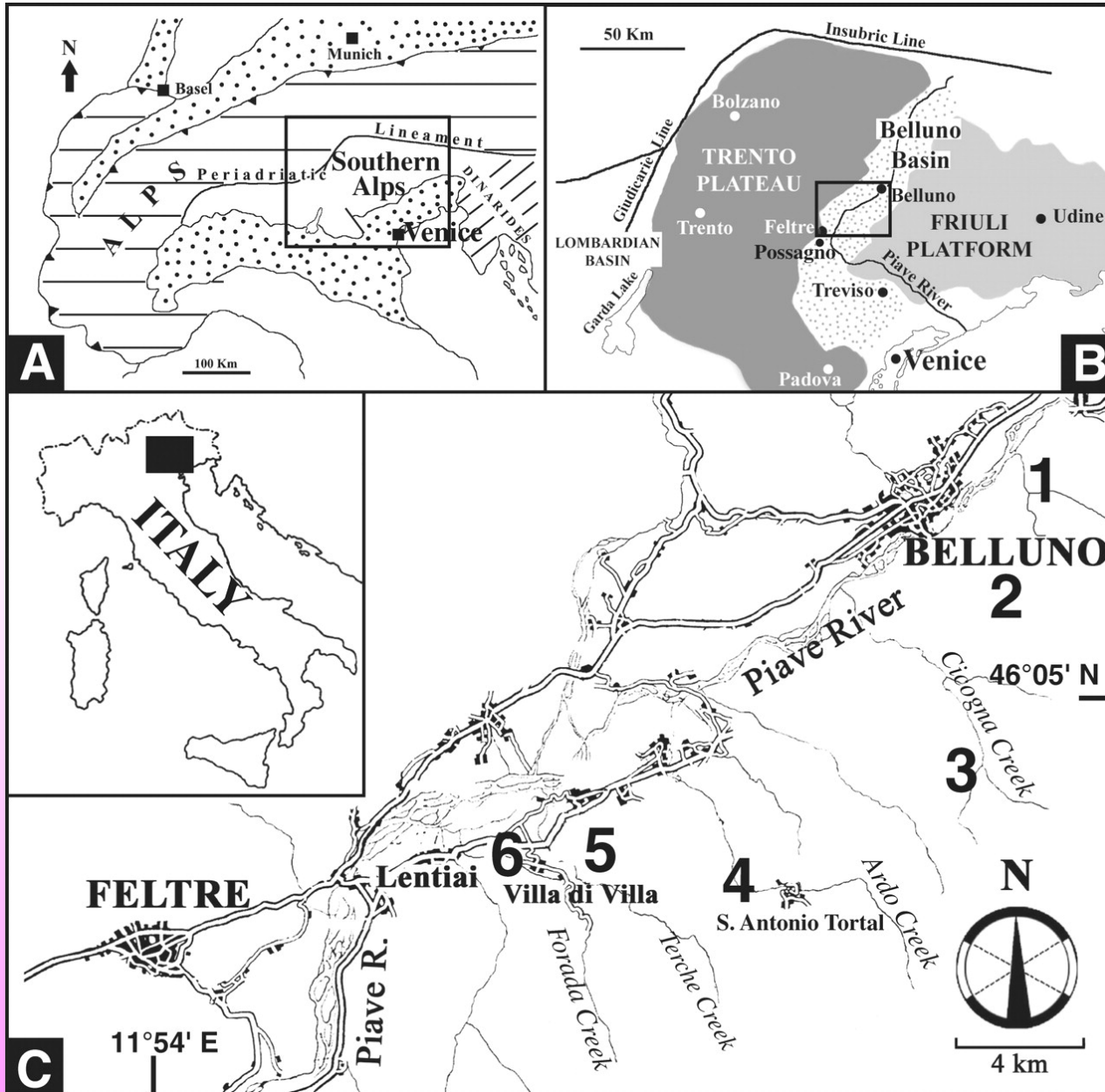


altered
physiology



less
calcification
increase of
malformations

THE TORRENTE FORADA SECTION



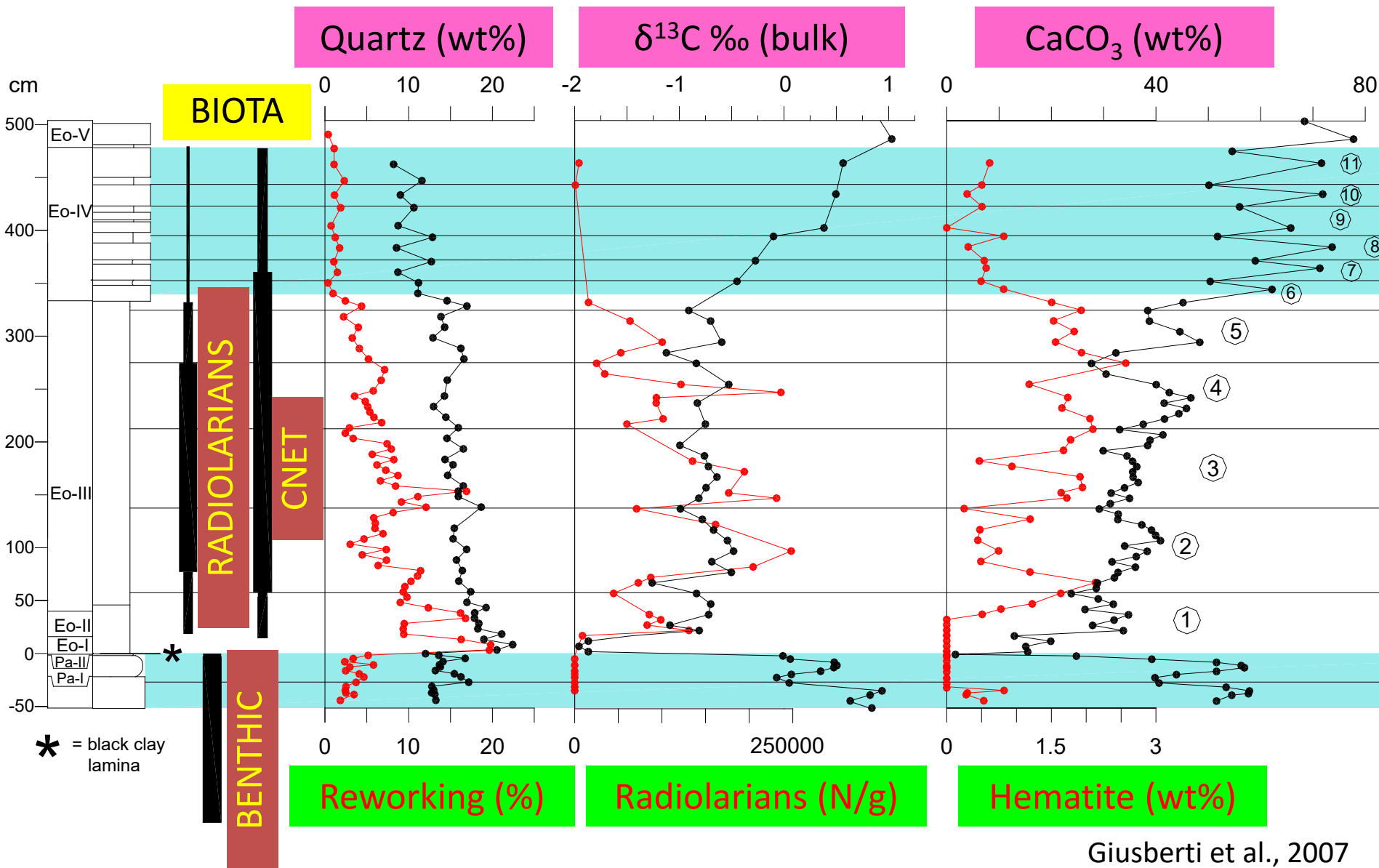
The PETM at FORADA

A black and white photograph of a geological outcrop. The upper portion of the rock face shows distinct, horizontally layered bedding. The lower portion is a darker, more uniform material. The foreground is cluttered with rocks, twigs, and some sparse vegetation.

**EOCENE COUPLETS
UNIT**

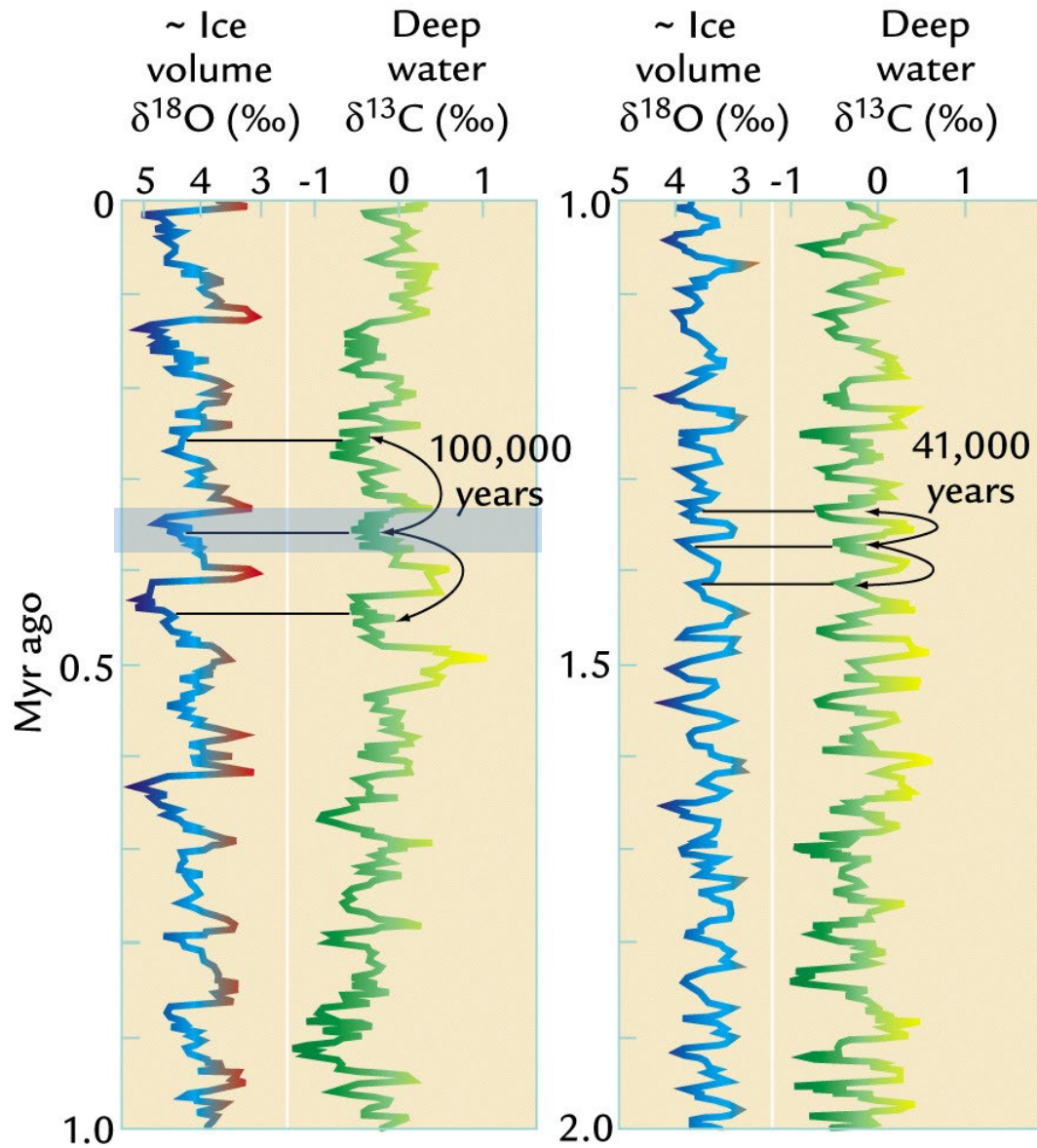
**CLAY MARL
UNIT**

Bio-geochemical proxies



$\delta^{13}\text{C}$ AT ORBITAL SCALE

$\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the PLEISTOCENE



Pleistocene isotope data in a Pacific cores (benthic foraminifera)

$\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ show a correlated pattern, though not flawless.

$\delta^{13}\text{C}$ is typically "lighter" during glacials, suggesting ^{12}C enrichment and more negative values.

What might account for this?

What could be the explanation for the $\delta^{13}\text{C}$ changes during the Pleistocene glacial-interglacial cycles ?

← Exit

Go to **wooclap.com** and use the code **PCCC2023**



What could be the explanation for the $\delta^{13}\text{C}$ changes during the Pleistocene glacial-interglacial cycles?

What could be the explanation for the $\delta^{13}\text{C}$ changes during the Pleistocene glacial-interglacial cycles?

1 biological productivity

2 carbon exchanges among reservoirs

3 ocean circulation

0% 0

0% 0

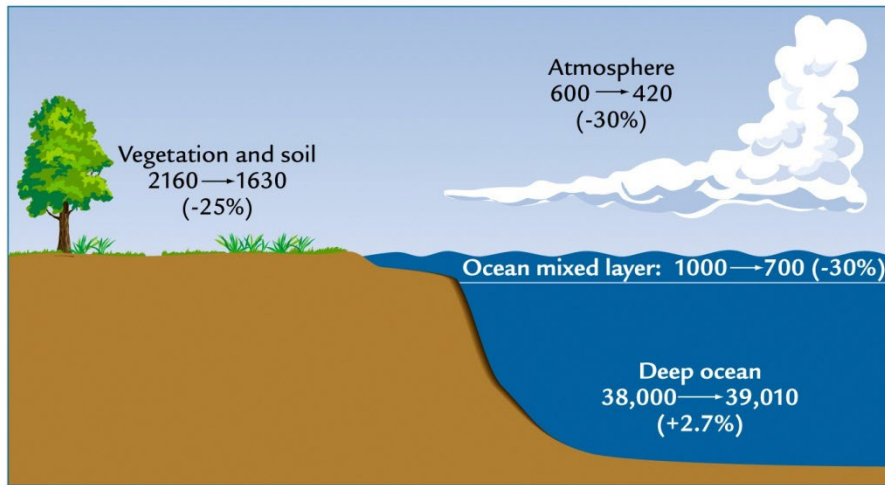
0% 0



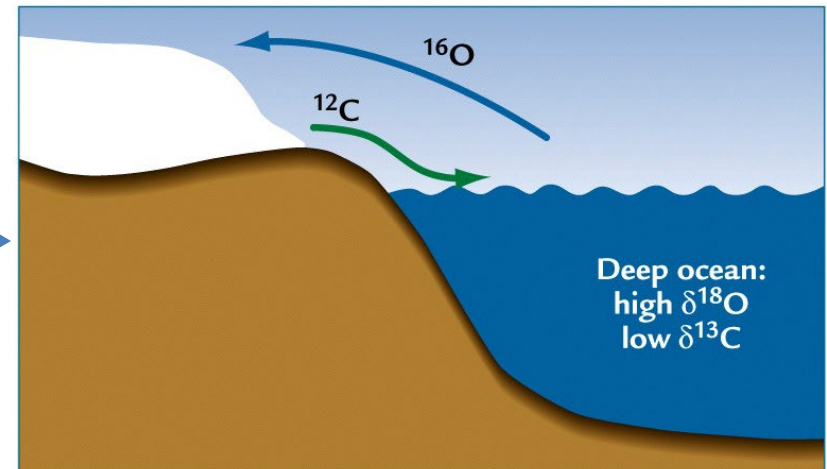
<https://app.wooclap.com/events/PCCC2023/0>

C reservoirs exchanges during glacials and interglacials

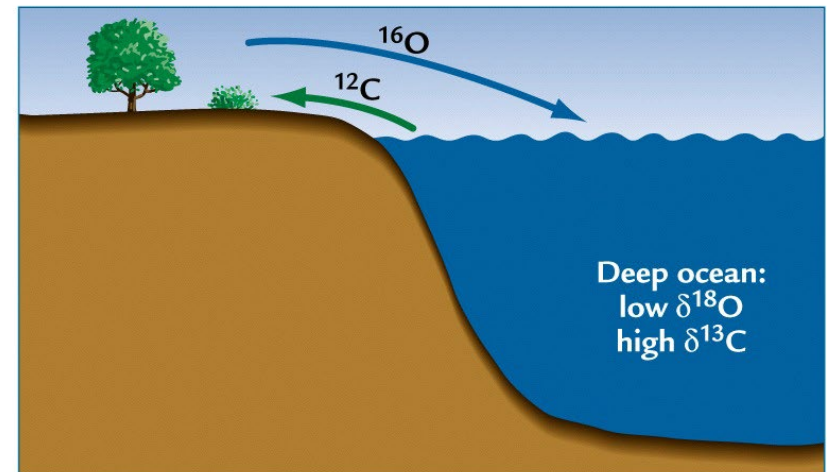
Carbon fluxes among reservoirs



$\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ variations during glacials and interglacials



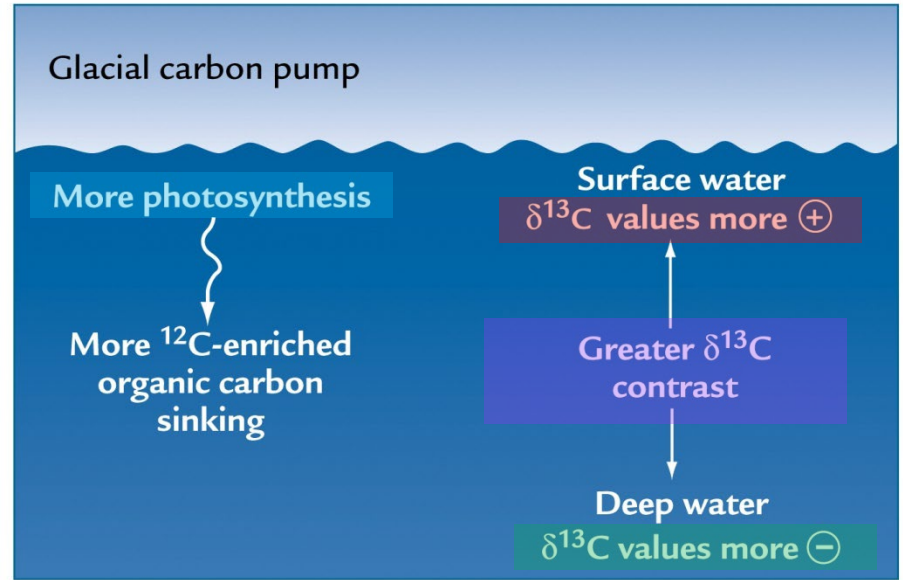
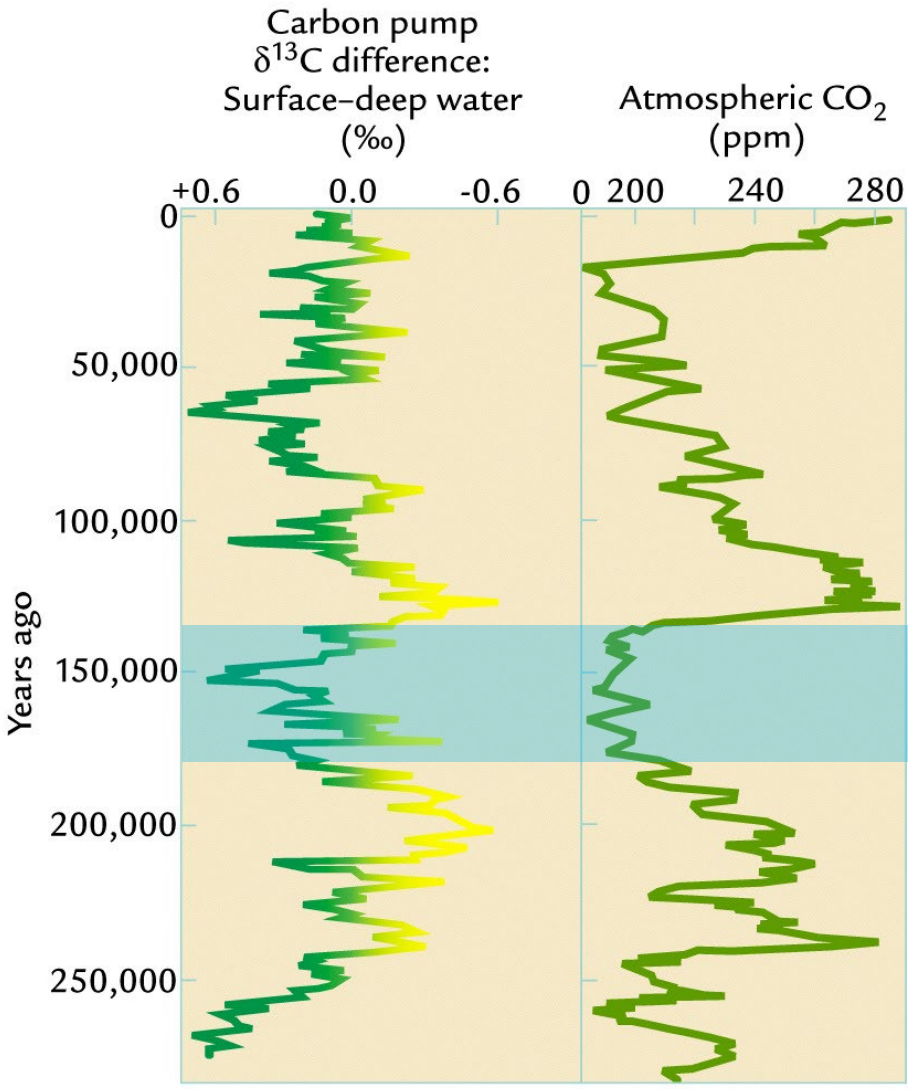
A Glacial climate



B Interglacial climate

In the Last Glacial Maximum (LGM), we witness ice-caps expanding at the cost of vegetation, steppe and tundra spreading towards lower latitudes, ultimately reducing terrestrial vegetation by around 25%.

$\Delta \delta^{13}\text{C}$ NEL GLACIALE: POMPA BIOLOGICA?



During glacials productivity is >

This results in a larger difference between
 $\delta^{13}\text{C}_{\text{surfacewaters}}$ e $\delta^{13}\text{C}_{\text{deepwaters}}$

So that

$\delta^{13}\text{C}_{\text{surfacewaters}}$ heavier

$\delta^{13}\text{C}_{\text{deepwaters}}$ lighter

PALEOENVIRONMENTAL SIGNIFICANCE OF $\delta^{13}\text{C}$ IN CARBONATES

The paleoenvironmental "signal" in $\delta^{13}\text{C}$ of carbonates, especially in planktonic and benthic foraminifera shells at a specific site, can be challenging to interpret, as it reflects:

- 1. Variations in $\delta^{13}\text{C}$ of TDIC in the oceans over geological time due to changes in carbon sinks.**
- 2. Local productivity (vertical and horizontal gradients).**
- 3. Global deep ocean circulation.**

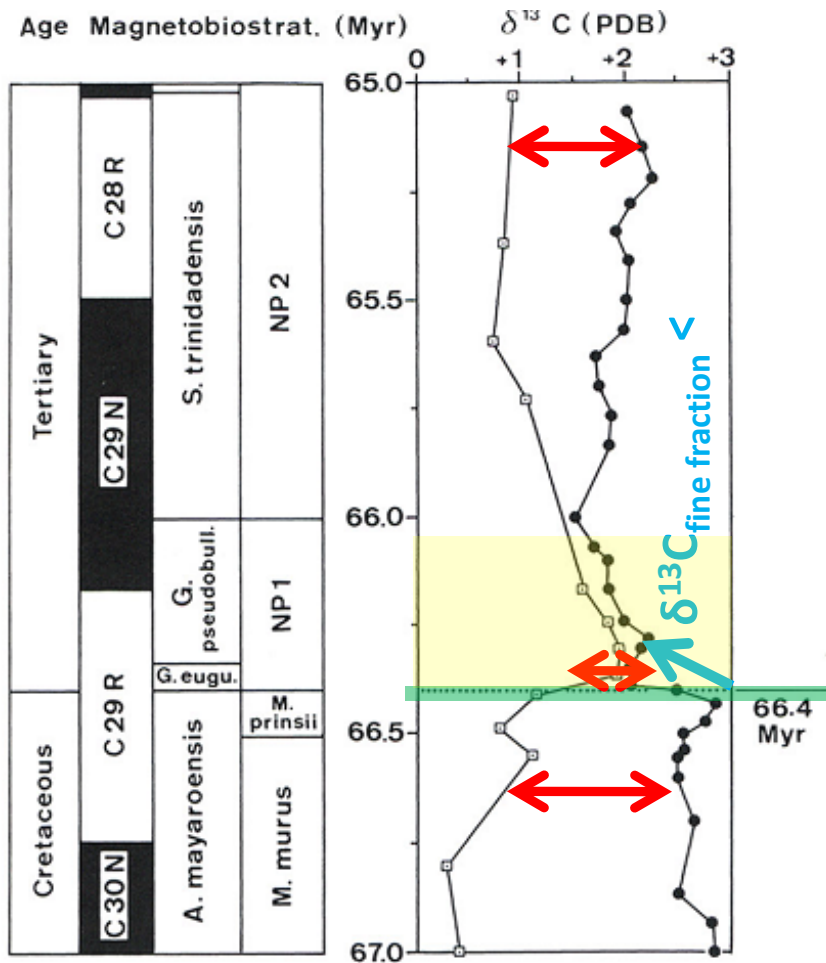
$\delta^{13}\text{C}$ AND MASS EXTINCTIONS

PREMISE

If we analyze the $\delta^{13}\text{C}$ record of the benthic and planktonic foraminifera of a sedimentary succession, we will observe an offset (**$\delta^{13}\text{C}$ vertical gradient**) between the two datasets but no variation in their absolute value of the gradient (**$\Delta\delta^{13}\text{C}$**) unless changes in productivity occur.

Conversely, if there are changes in biological productivity or changes in ocean circulation (we leave out this complication), changes in the gradients between the $\delta^{13}\text{C}$ of planktonic and benthic foraminifera (**$\Delta\delta^{13}\text{C}$**) will be observed. The most dramatic case of rapid change in biological productivity can occur during mass extinctions such as that at the K/T (K/Pg) boundary.

CASE STUDY : The K/T o K/Pg



Zachos et al., 1989

- Fine fraction (nannoplankton)
- R. rotundata, DSDP 577 (foraminifero bentonico)

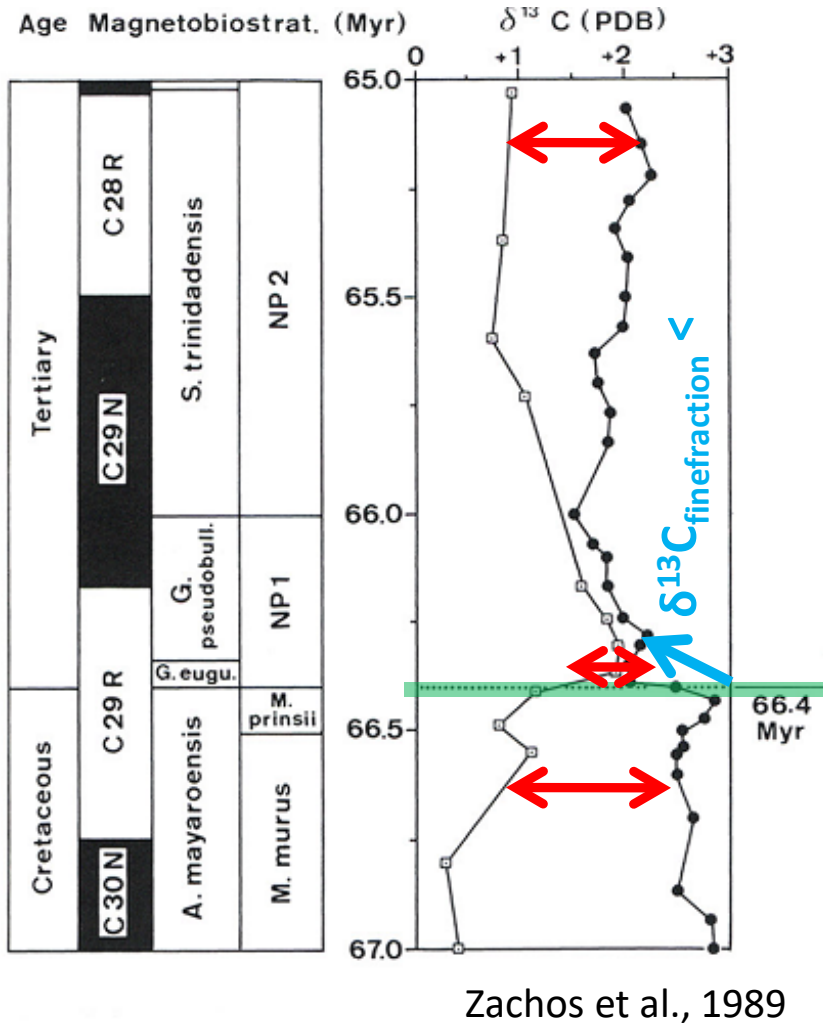
In the figure the $\delta^{13}\text{C}$ variations in benthic foraminifera (□) and fine fraction (●) are reported. The $\delta^{13}\text{C}$ of the fine fraction, consisting of coccoliths, “reflects” the isotopic values of the TDIC of surface waters.

During the Maastrichtian and the Paleocene the $\delta^{13}\text{C}$ gradient between the fine fraction and the benthic is $> 1\text{‰}$ \rightarrow oceanic conditions are “normal” (similar to the modern ones).

At the K/Pg boundary (Ir anomaly) and for a few hundreds of thousands of years in the Paleocene we have that:

- 1) the $\delta^{13}\text{C}$ values of the fine fraction become more negative
- 2) the vertical gradient of $\delta^{13}\text{C}$ vanishes.

THE "STRANGELOVE OCEAN" (Hsü et al., 1985) after Dr. Strangelove (Kubrich's movie)



● Fine fraction (nannoplancton)

◻ R. rotundata, DSDP 577 (foraminifero bentonico)

To explain these data:

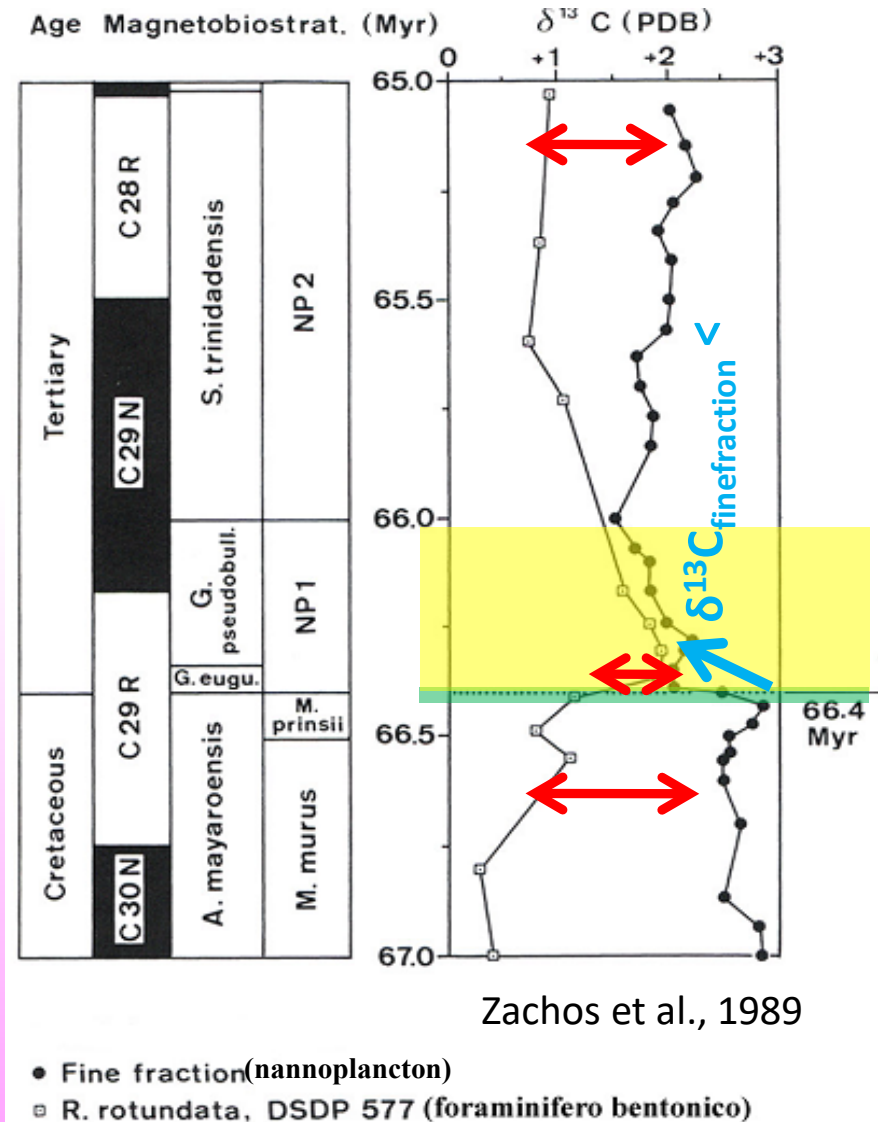
- 1) release of "light" carbon from the biosphere to the oceans (think of the virtually non-existent vegetation after the event) and
- 2) a collapse of primary biological productivity linked to the nuclear winter caused by the impact of an asteroid (remember Yucatan), which leads to canceling the $\delta^{13}\text{C}$ gradient between the surface and the ocean floor.

The values of $\delta^{13}\text{C}$ testify the collapse of primary productivity following the K / Pg catastrophe (asteroid impact). The situation remains abnormal for a short time.

THE "LIVING OCEAN"

In reality, explaining the anomalous conditions in the plankton-benthos $\delta^{13}\text{C}$ gradient can be more complex. This anomaly persists long after the impact event, and life quickly recovers, making it unlikely that there was no biological productivity in the upper ocean for nearly a million years (see the figure).

Many scientists attribute this anomaly not to a lack of surface water productivity but to a limited supply of organic matter on the seafloor. In other words, photosynthesis returns to normal, but the insufficient organic matter oxidation maintains the low or zero gradient (preventing DIC values from returning to their original "light" state). The details are extensive and beyond our scope. However, the key takeaway from these findings is that mass extinctions, like the K/Pg event, impact both organism biodiversity and the stability of natural ecosystems. Another hypothesis involves changes in the vital effect of benthic foraminifera (Henahan).



$\delta^{13}\text{C}$ NELLE ALTRE ESTINZIONI DI MASSA

Anomalies of $\delta^{13}\text{C}$ are also present in many other mass extinctions and in “environmental upheavals”, such as those in the terminal part of the Precambrian (Neoproterozoic).

