Maurice Huguenin-Virchaux

Organic Geochemistry and the Global Carbon Cycle

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Week 1 – An Introduction to the Carbon Cycle

1

Definitions:

- net primary production → NPP
- gigaton ≙ 10^9 g → 1 gigaton = 1000 Tg = 1 Pg = 0.001 Eg
- teragram ≙ 10^{12} g
- petagram ≙ 10^{15} g
- exagram ≙ 10^{18} g
- OM = organic matter
- more refractory = more likely to be preserved
- Kerogen
  - mixture of organic chemical compounds that make up a portion of the organic matter in sedimentary rocks
  - insoluble in normal organic solvents because of the high molecular weight of its component compounds.
- ℃

What are organic Geochemists interested in? From Emerson and Hedges (1988):
"Marine sediments as the primary long-term repository of organic matter and thus provide the most complete record of life on Earth and represent an important source of fossil fuel."

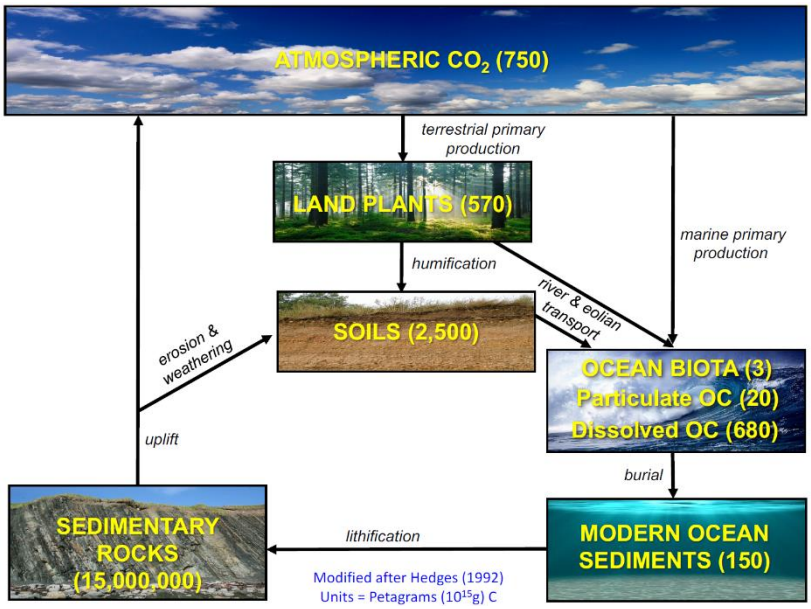
Interests of organic chemists

- **reconstruction of paleoenvironments**
  - climate
  - primary productivity
  - source inputs
  - depositional environments
- **biological evolution** → concept of "chemical fossils" or "biomarkers" for interpreting the fossil record
- understanding the role of **reduced carbon** (OM) on continents, atm. and in the oceans
- **origin of petroleum** source rocks and coal deposits

Gaia Hypothesis → all organisms and their inorganic surroundings on Earth are closely integrated, form a single & **self-regulating** complex system & maintain conditions for life on the planet (i.e. thermostat)

The global organic carbon cycle

- "active reservoirs" between atmosphere, land plants and ocean
- "inactive reservoirs" between deep ocean and sedimentary rocks
- **where** does the **CO_2** go?
  - **40%** remain in the **atmosphere**
  - **30%** taken up by **land** cover
  - **30%** taken up by the **ocean**



Overview of global carbon inventories (reservoirs) → Figure to the right

a) Sedimentary (rock) reservoir

- **main** reservoir of carbon in the Earth's crust
- they hold 15,000 * 10^{18} g organic carbon
- sedimentary organic carbon primarily in shales (71 %), carbonates (14 %) and sandstone (10 %)
- the primary form of organic carbon in these deposits = **KEROGEN** (i.e. finely disseminated, solvent-insoluble organic matter)
- although by far the largest reservoir, turnover very slow → geological timescales

b) Surface pools

- although smaller, reservoirs numerous and more dynamic
- dissolved inorganic carbon (**DIC**) in seawater is the largest (ca. 40*10^{18} gC) → more than one magnitude larger than all other surface pools
- four largest organic carbon reservoirs:
  - surficial **soil** "humus"
  - terrestrial **plant** tissue
  - non-living organic **carbon in seawater**
  - organic matter in **mixed layer** surface **sediments**
- non-living organic matter in seawater includes both dissolved (DOC) and particulate (POC) organic carbon
  - DOC ≙ ~95 % of the total amount of non-living carbon in seawater
- organic carbon content of living marine organisms is trivial compared to DOC and POC

Overview of global **carbon fluxes → all estimates**

- **weathering** of kerogen in continental rocks → currently no accurate data
- terrestrial **primary production** → NPP estimated to be around 50 * 10^{15} g C yr^{-1}
- **riverine input** to the oceans → is ~0.5 % of global terrigenous primary production
- **eolian** transport → i.e. transport by the winds, hard to estimate since few measurements of average total flux to the seas
- marine **primary production** → 60 – 80 % in the open ocean and estimated 50 * 10^{15} g C yr^{-1}
- **dissolved organic carbon** (DOC) flux → estimated 0.1 * 10^{15} g C yr^{-1}
- **particulate flux** → POC sinking below ca. 100 m in the oceans estimated ~ 7 * 10^{15} g C yr^{-1} and is equivalent to ~15 % of total photosynthetic production
  - flux is ~1 % of the marine photosynthetic production as particles sink from 100 m to the deep ocean
- **sediment burial** → very efficient recycling/ remineralization of organic matter in the water column, flux estimated 0.1 * 10^{15} g C yr^{-1}, therefore at most 4 % of the particulate flux in the euphotic zone is buried in marine sediments

Overview of global carbon fluxes:

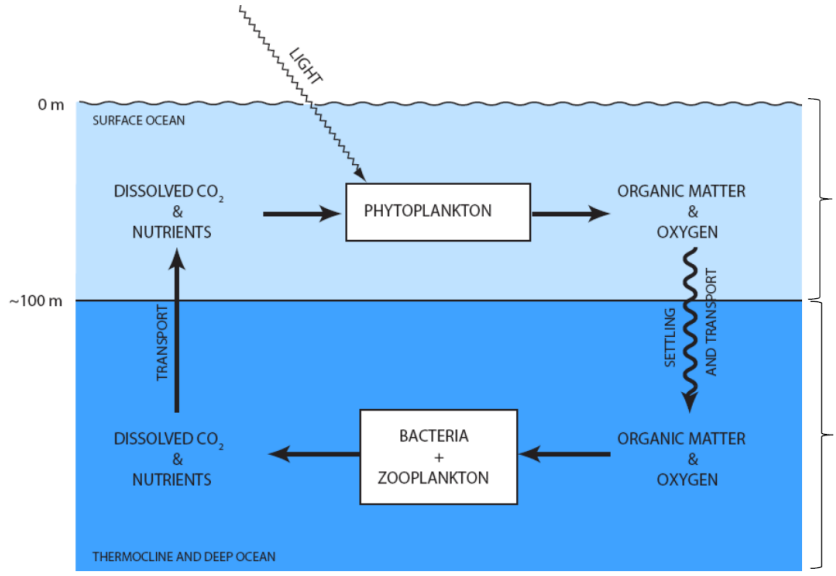
- *weathering of kerogen in continental rocks*
- *terrestrial primary production*
- *riverine input to the oceans*
- *eolian transport*
- *marine primary production*
- *dissolved organic carbon flux (DOC)*
- *particulate flux*
- *sediment burial*

The observation that ca. 0.1 % of the global NPP is ultimately preserved in sediments attests to the extreme efficiency of remineralization in the upper ocean.

Dissolved and Particulate organic matter (DOM, POM)

- majority of organic matter supplied to marine sediments delivered in the form of rapidly **sinking particles**
- DOC does not contribute significantly to the sedimentary organic carbon pool
- most of the vertical flux from the surface ocean believed to be in the form of macroscopic entities (e.g. fecal pellets and large amorphous **aggregates** ("marine snow") supplied via the biological pump

The **biological pump**: carbon export to the deep ocean



ocean flux:

biomass
↓
sinking POC
↓
mesopelagic realm
↓
bathypelagic realm
↓
marine sediments

land the flux:

biomass
↓
leaf litter
↓
soil (transport via fluvial realm)

- big **spatial** / geographic and **temporal variability in fluxes** of both land and ocean biomass over the Earth's surface
- **freshwater discharge** from the continents (and subsequent sediment input to the ocean) **mainly** in **South America** (Amazon river) and **Southeast Asia** region (monsoon)
- 40 – 70 % of the sediments delivered to the oceans is transported by numerous small rivers → these systems transport OC that is distinct in composition from the world's largest and better studied rivers

Distribution of organic carbon in marine surface sediments

- **deposition** mostly along **continental margins** and in river **delta** regions
- approx. **80 %** of global organic carbon burial within deltaic/continental shelf env.
- comparatively little organic carbon accumulates in pelagic or euxinic (low-/no oxygen) environments

→ this mainly a consequence of

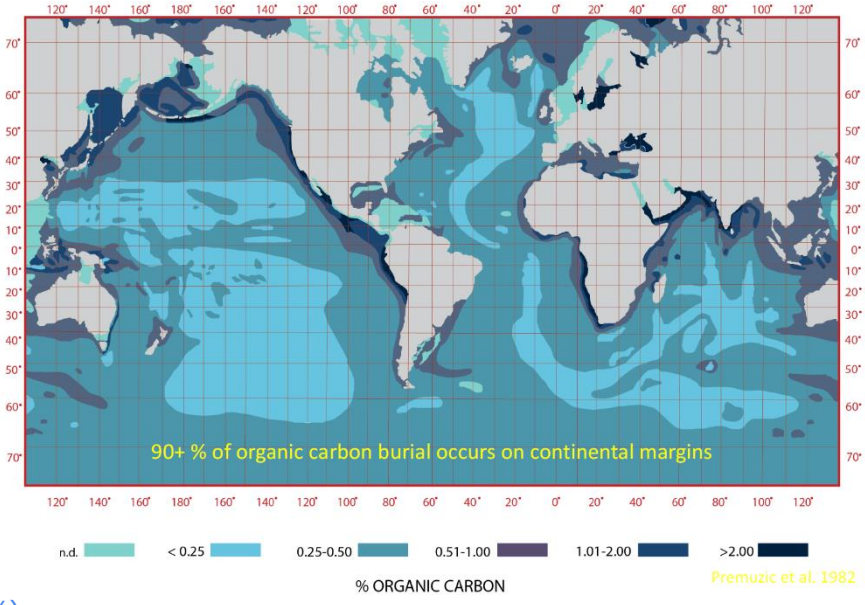
a) **higher productivity** of the overlaying waters
b) **higher sedimentation** rates

- remineralization greater in the open ocean (80 – 90 %) compared to near-shore/upwelling regimes (ca. 50 %)

→ this is due to

a) **longer, oxygenated water column** in the open ocean and
b) **slower sedimentation** rates

- different values for burial in mixed-layer surface sediments of the continental margin and of the abyssal ocean due to **bioturbation** and the quality of organic matter reaching the sea floor → bioturbation, i.e. mixing by living species, mixes the sediment and leads via turbulence to upward carbon flux



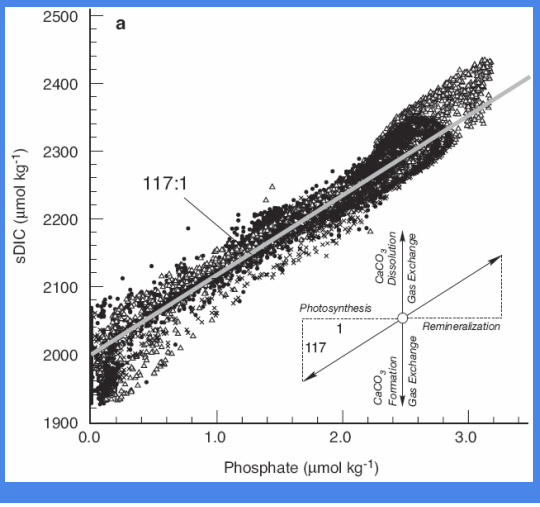
- **terrestrial organic matter more refractory** than marine organic matter (i.e. more likely to be preserved): **~50 %** of the marine carbon burial **flux** comes **from the continents**

Sources of organic matter

- organic matter in marine sediments either from **marine or terrestrial origin**
- **marine-derived** organic matter = "autochthonous" → produced essentially in-situ
  - mainly phytoplankton in the upper 100 m of the surface ocean
  - zooplankton
  - bacteria
  - archaea
- **heterotrophic** (utilize pre-formed organic carbon)
- **autotrophic** → i.e. organism produces compound from simple substances present in its surroundings
  - photosynthetic
  - chemosynthetic → organism produces carbon substances via chemical reactions, not that large on global scale, but can be substantial locally, i.e. at vents
- **land-derived** organic matter → "allochthonous"
  - recent plant debris
  - dissolved soil substances

Redfield concept of constant stoichiometric ratios

- composition of organic matter C:N:P:O_2 ≈ 106: 16: 1: -150
- remineralization below 400 m C:N:P:O_2 ≈ 117: 16: 1: -170



Composition of source organic matter

- composition of **oceanic sources, i.e. plankton**
  - phyto- & zooplankton contain wide variety of biochemicals
  - particularly rich in proteins
  - overall ratio **C: N: P: O_2** → ("Redfield Ratio" in box)
- composition of **terrestrial sources**
  - structural biochemicals important to support plant in air
  - terrestrial plant tissue can be sub-characterized as
    - woody biomass (ca. 75 %)
    - non-woody biomass (e.g. leaves, grasses, ca. 15 %)
    - litter
  - low nitrogen content (i.e. high C/N ratio)
  - huge mass of woody tissues in terrestrial biomass makes **cellulose** (40 % of wood), **hemi-cellulose** and **lignin** (each about 25 % of wood) the **most abundant polymers on Earth**
    → the monomer **glucose** is arguably the single **most plentiful biochemical** globally
  - soil organic matter consists primarily of remains of vascular plants and includes humic substances as well as base-insoluble organic matter (humin)

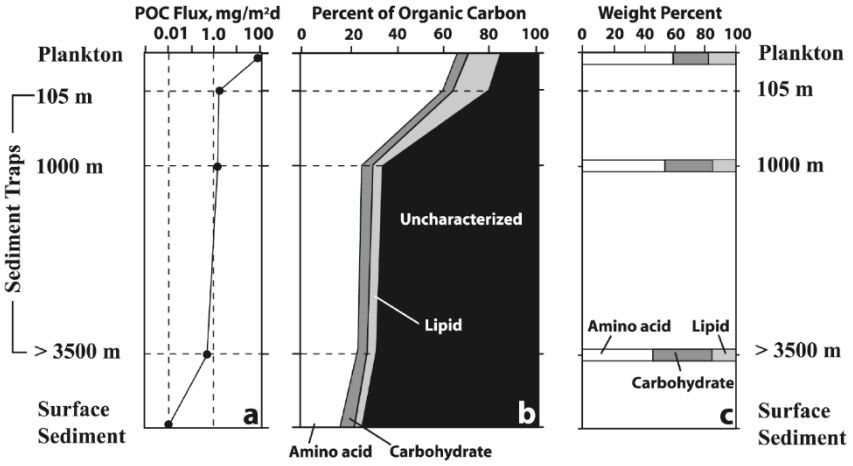
Some important considerations

- organic compounds synthesized by organisms are subject to biological and physiochemical processes that alter their chemical composition (e.g. oxidation) → this complicates their recognition and quantification in downstream organic carbon reservoir such as soils & sediments

  - modification of organic matter = “pre-conditioning”
- the time scale, over which OM is processed may vary substantially, depending on its origin
- cont. margins contain significant quantities of “pre-aged” organic matter

Building blocks of biomass and sedimentary organic matter → picture to the right

- flux down is one order of magnitude smaller (~1 %) and **burial rate even more small (~0.01)** → only a fraction of organic matter is eventually buried in the sediment
- uncharacterized OC increases with depth, we do not know anymore its origin since it gets altered



Take – Home messages:

- **sediment**ary rocks = **largest reservoir** of reduced carbon in the Earth’s crust
- **remineralization**, i.e. oxidation of OM back to CO_2, nutrients and water, by far the **most common fate** of recently biosynthesized carbon
- **much of focus** of organic geochemistry **on** the **small remnants** of OM from marine & terrestrial production **that escapes remineralization**
- vast majority of organic **burial within deltaic/continental shelf** and, to much lesser extent, upwelling regions
- smaller, but much more reactive pools of OC in the oceans, play more important role in short-term carbon cycling than sedimentary rocks
- **POM** represents the **major mode of supply** or OM **to** marine **sediments** → through the biological pump
- due to significance of organic carbon burial on cont. margins, **land-derived OM** may potentially be a **significant source** for OC in marine sediments
- bulk chemical **composition of marine vs. terrestrial** OM is markedly **different** → should be reflected in sedimentary OC compositions
- we are presently unable to fully chemically characterize sedimentary organic matter

key questions for exam: see last few slides week1_Introduction

Week 2 – The long-term Carbon Cycle

2

Goal:

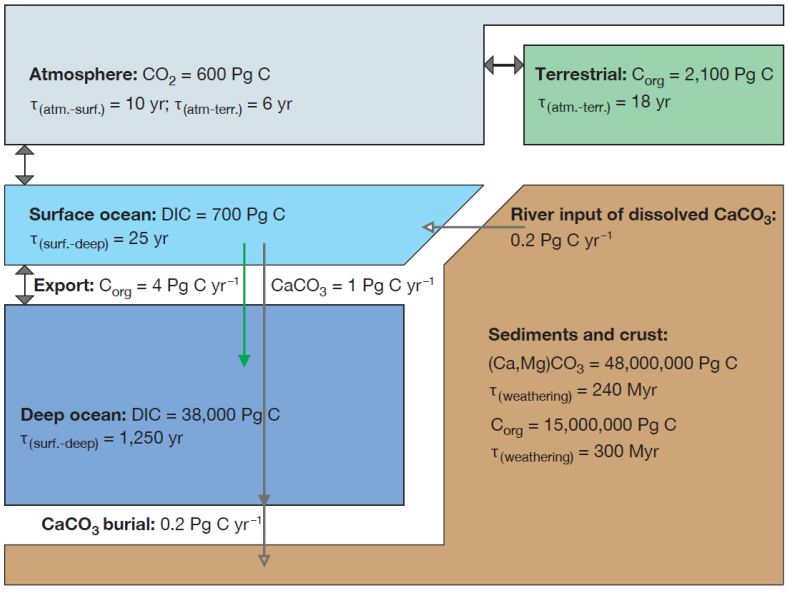
- emphasize and illustrate the role of rivers in the long-term organic carbon cycle

The **short-term** carbon cycle
→ from few months (interseasonal) to millennial-scale variability

- exchange of carbon on human time scales → Mauna Loa CO_2 & O_2/N_2 record
- exchange of carbon on glacial-interglacial time scales → ice core records

The **long-term** carbon cycle
How is pCO_2 measured beyond the ice core record?

a) **fossil leaves stomatal density** & carbon **isotopic composition** of $\delta^{13}C$ (species dependent – needs calibration)



b) **isotopic composition** of carbonates and organic matter in **paleosols** (also dependent to some extent on soil formation and temperature)
c) **isotopic composition of $\delta^{11}B$** (Boron) incorporated in marine organisms (dissolved $\delta^{11}B$ in the ocean is a function of ocean pH, which is in turn a function of $pCO_2^{atm.}$)
d) **box model approaches** (parametrisation the exchange of C between reservoirs)

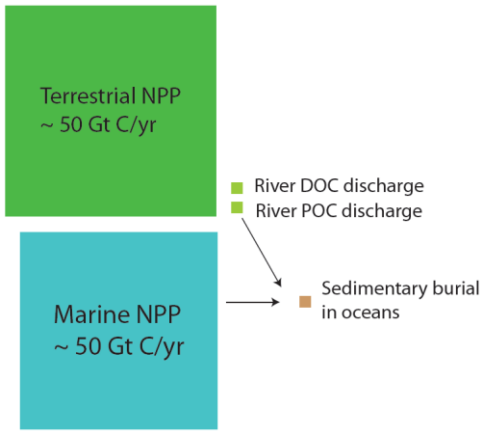
- imbalances in the exchange between Earth's surface carbon reservoirs and Earth's crust = long-term carbon cycle
- need to account for carbon exchange between sedimentary & atmosphere-ocean-land-systems

The organic side

- organic carbon transport and burial

$$6H_2O + 6CO_2 + hv \rightarrow photosynthesis \rightarrow C_6H_{12}O_6 + 6O_2$$
$$\rightarrow transport\ \&\ burial \rightarrow kerogene, coal, \ldots$$

- organic carbon **burial** is a "**small leak** in the short term carbon cycle"
- ~90 % of the total marine OC burial occurs on continental margins where we have a lot of bioproductivity
- furthermore, cont. margins are strongly influenced by terrestrial inputs from rivers
- terrestrial POC flux is sufficient to account for all OC being buried in marine sediments



The inorganic side: chemical weathering reactions

- in the long-term carbon cycle both carbonate/silicate and organic carbon cycles must be considered
- weathering of (Ca/Mg)-Silicates removes CO_2
- weathering of carbonate rocks is CO_2 neutral (i.e. CO_2 gets removed but is rereleased again)

- **silicate weathering** of (Ca/Mg)-Silicates **removes CO_2** from the atmosphere
  → substitution of Ca^{2+} with Mg^{+} possible

$$3H_2O + 2CO_2 + CaAl_2Si_2O_8 \rightarrow Al_2Si_2O_5(OH)_4 + Ca^{2+} + 2HCO_3^- \rightarrow Ca^{2+} + 2HCO_3^- + CaCO_3 + CO_2 + H_2O$$

- silicate weathering transfers carbon from the atmospheric to the geological reservoir

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2$$

- the role of non-Ca and Mg silicate weathering in the carbon cycle is more complex → weathering of Cl^-, H_4SiO_4, SO_4^{2-}, K^+ silicates not really with an impact on overall cycle
- **weathering of Na and K** silicates consumes CO_2, but this **CO_2** is not stabilised as carbonates but most likely **re-emitted** to the atmosphere during "**reverse weathering reactions**":

silica + degraded aluminous clays + Fe_2O_3 + organic carbon + soluble cations + HCO_3^-
↓
new clay material + CO_2 + H_2O

- on long time scales and at steady state, **weathering of carbonate rocks** is carbon **neutral**:

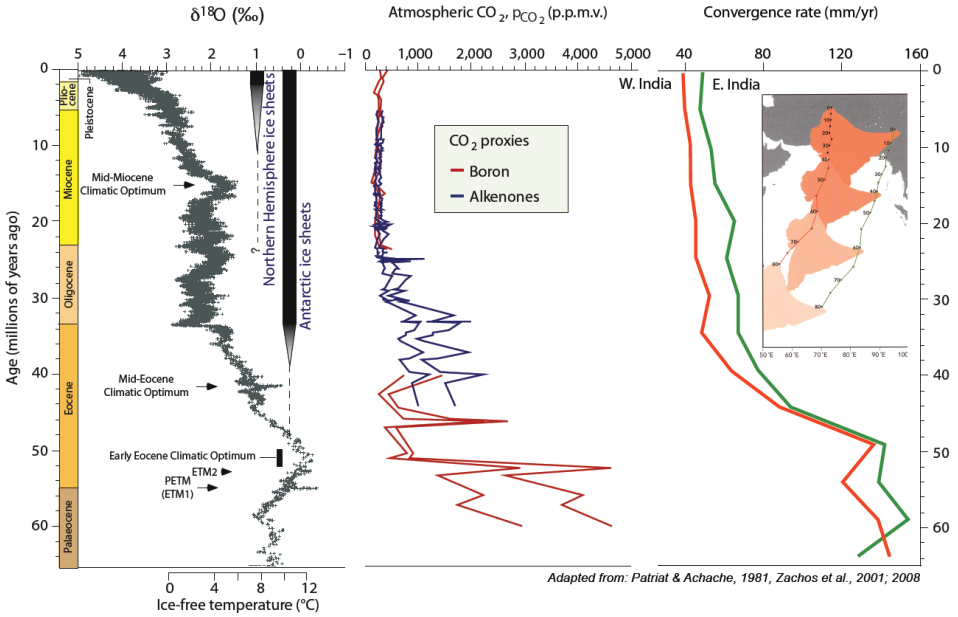
limestone weathering: $CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$
limestone precipitation: $Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O$

Return of carbon from the sedimentary record into the atmosphere

- recycling back to the atmosphere in subduction zones
  - ~90 to 95 % of total carbon subducted is inorganic (sedimentary carbonate and low temperature crust alteration carbonates)
  - **~50 %** of total **carbon** subducted **returns to the atmosphere** directly within the **volcanic arc**
- **oxidation** of sedimentary OC in **surface processes** transfers geologic or stabilised carbon to the atmosphere (e.g. during continental collision)
- decarbonation of carbonates at high temperatures leads to outgassing → e.g. at hot springs

Uplift and weathering/carbon burial as controls of long-term climate

$$\delta^{13}C\ (‰) = \left[\frac{\left(\frac{^{13}C}{^{12}C}\right)_{sam} - \left(\frac{^{13}C}{^{12}C}\right)_{std}}{\left(\frac{^{13}C}{^{12}C}\right)_{std}} \right] \cdot 1000$$



Balance between organic and inorganic carbon reservoirs through time

- $\delta^{13}C_{mantle}$ ~ **- 5 ‰**
- fractionation between carbonate rocks and organics: $\delta^{13}C_{carbonates} - \delta^{13}C_{organics}$ ~ **- 25 ‰**
- mass balance equation: $\delta^{13}C_{carbonates}$ * **X** + $\delta^{13}C_{organics}$ * (1-**X**) = $\delta^{13}C_{mantle}$
- $\delta^{13}C_{carbonates}$ ~ **0 ‰**

- 82 % of the carbon is in carbonates
- 18 % of the carbon is in organics
- global carbon burial rate changed considerably through time (dependent on surface area/tectonic processes)
- more recent global carbon cycle models take more parameters and records into account such as
  - chemical weathering records ($^{86}Sr/^{87}Sr$; $^{187}Os/^{188}Os$; ...)
  - mantle degassing (volcanic eruptions, spreading rate at ridges, ...)

Take – Home messages: long-term carbon cycle

- long-term pCO_2 in the atmosphere controlled by exchange of carbon with slow cycling carbon pools: Earth's crust
- OC burial and silicate weathering are two important parts of this inorganic carbon cycle
- models and paleo-records are useful to reconstruct long-term carbon cycling over longer time-scales but major discrepancies remain
- understanding what flux of carbon leaves the short-term cycle and is transferred to the geological record is key

Rivers and the organic carbon cycle

- rivers: main carbon conveyor belts from the continents to the oceans
- riverine organic carbon transport as
  - DOC: dissolved organic carbon → not collected on filters: < 0.2 / 0.45 / 0.7 µm
  - POC: particulate organic carbon → collected on filters: < 0.2 / 0.45 / 0.7 µm

DOC

- very diverse organic molecules: humic & fulvic acids, humin, ...
- less important for long-term carbon cycle
- rapidly re-mineralised on continental margins and in the ocean (average DOC turnover in the oceans: 4000 to 6000 years) → most relevant to the short-term carbon cycle

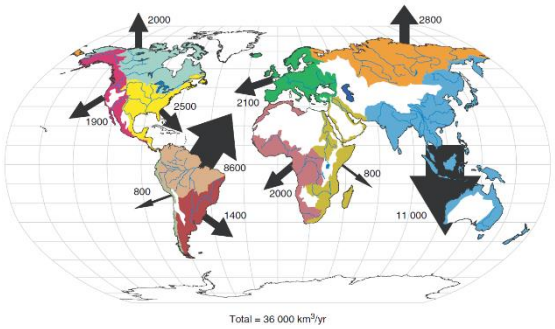
POC

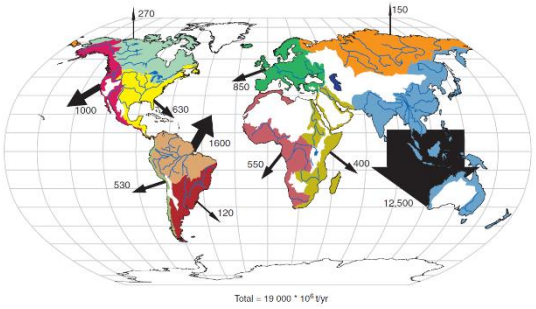
- strongly associated with the sediment load
- from m- to sub-µm scale
- may contain whole plants, even tree trunks which are really good records

- the higher the surface area, the more POC may attach at the surface, e.g. clays with high surface area & high POC concentrations
- C_{org} preservation and stability is linked to mineral / organic matter associations

River POC flux = river discharge * concentration

- equatorial rivers dominate POC discharge into the oceans (figure to the right: numbers are mean annual discharge in km^3/year, the arrows are proportional to these numbers
- global sediment flux dominated by Southeast Asia with monsoon and volcanos that have high erosion rates
- the above approximation (**flux** = discharge* conc.) **not so easy** to determine since
  - sediment flux data is scarce → e.g. no sediment flux measurements in Ganges-Brahmaputra region
  - bedload flux is poorly quantified
  - POC fluxes require additional %C measurements on sediment samples
  - temporal variability high and depending on region





Global fluvial discharge above - Global sediment flux below

from before:

- transfer & subsequent burial of modern POC = **carbon sink**
- transfer & oxidation of fossil or petrographic POC = **carbon source**

→ thus understanding controls on the nature of POC export in rivers important for better understanding of the global carbon cycle

- we want to know not only how C_{org} is transferred to the rivers but also what kind of C_{org}

River heterogeneity

- riverine POC is a mixture of fossil / petrogenic and modern carbon
- elemental composition (N/C), stable isotopic composition ($\delta^{13}C$) and radiocarbon content ($\Delta^{14}C$) allow tracing the source of POC
- **POC fluxes** are **difficult** to constrain → estimates need to **take into account** spatial and temporal **variability of** the organic carbon **loading and composition**

Mobilisation of POC

- river C_{org} discharge = f(erosion, transport, climate, ...)
- erosion: harvesting or organic carbon in the landscape
  - e.g. Taiwan as erosional "hot spot" with river POC =
    - 70 % bed-rock/fossil POC
    - 30 % modern carbon
    - river sampling during a typhoon, %C content and ^{14}C measurements → use of radiocarbon to partition POC between modern and fossil
    - **80 to 90 % of modern POC is exported during** these **extreme events**
    - coarse woody debris exported during typhoon Morakot (2009) = 10 to 26 % or the yearly POC export from the Amazon
  - most sediment transport by these extreme events → water with so much sediments that it is heavy & sinks in the ocean, i.e. an efficient way to sediment
  - fast transfer of POC also limits the oxidation of fossil POC in Taiwan (i.e. stabilizes carbon in the geological reservoir)
  - the contribution of modern, non-fossil POC increases with flow regime → that means: the bigger the river the more modern POC it transports (e.g. Amazon river with a lot of wood)

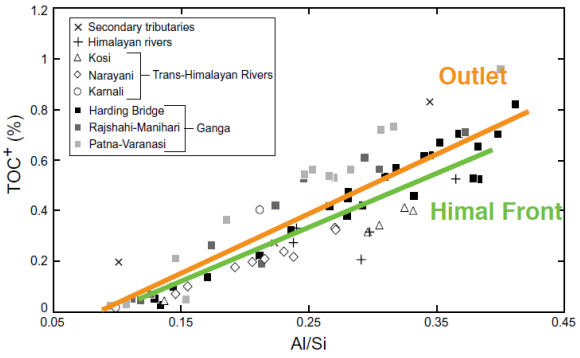
→ direct role of precipitation and runoff in supplying modern POC to the channels at the continental margins

- physical processes largely control the export flux and quality of POC in upstream landscapes

Transfer of POC in the fluvial system

- rivers as chemical reactions

- recycling of POC during riverine transfer, e.g. in the Himalaya
- POC loading increases with Al/SI ratio of the sediments (Al/Si ~clay vs. sand content)
  - change in $\delta^{13}C$ POC signature during floodplain transfer (figure to the right: Ganges river)
- **oxidation** of 50 to 70 % of **graphite/fossil POC** during transfer through **flood planes**: **CO_2 source**



Deposition of POC

- very high sediment accumulation rates in the Bengal fan
- efficient burial of POC in the Himalayan system
- sediment accumulation rates has a strong control on riverine POC preservation in the sedimentary cycle

Take home messages: rivers and the organic carbon cycle

- transfer of carbon from the continents to the oceans where it may be stored over geological time scales
- rivers can be used to quantify fluxes of carbon export
- not only conveyors but also "transfer functions" and "reactors" → important to understand the controls on continental carbon export but also to understand where molecular proxies are harvested in the landscape and how they are transferred (see week4_Biomarkers)

Week 3 – Radiocarbon and ^{14}C systematics

3

Reminder: isotopes with similar chemical species but with a different number of neutrons

- **^{14}C true half-life: 5730 years**
  - Meanlife, τ (8033 yr for the Libby half-life):

$$t_{1/2} = \tau \cdot ln(2)$$

  - Decay constant, λ (1.24×10^{-4} yr^{-1} for the half-life):

$$t_{1/2} = {ln(2)}/{\lambda}$$

name	stability	abundance	composition
^{12}C	stable	0.99	6 p + 6 n
^{13}C	stable	0.01	6 p + 7 n
^{14}C	radioactive	10^{-12}	6 p + 8 n

Radiocarbon production in the atmosphere

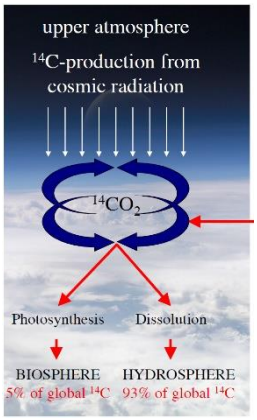
- cosmic rays → from the sun or outside the solar system interact with the atmosphere & produce a cascade of particles (electrons, neutrons, protons, ...)

$$^{14}N + neutron \rightarrow {}^{14}C + proton$$

- ^{13}C and ^{17}O can also form ^{14}C but very low rate due to their scarcity

nuclear reactions	chemical reactions
• p + N, O, Ar → n + ... • n + ^{14}N → ^{14}C + p	• $^{14}C + O_2 \rightarrow {}^{14}CO + O$ • $^{14}CO + OH^* \rightarrow {}^{14}CO_2 + H^*$ • $^{14}CO_2$ then to ATM, BIO & HYDRO

- ^{14}C production in the upper atmosphere, reacts to $^{14}CO_2$ → photosynthesis & dissolution leads to uptake by the biosphere and hydrosphere
  - **ATMOSPHERE: 2 % of global ^{14}C**
  - **photosynthesis → BIOSPHERE: 5 % of global ^{14}C**
  - **dissolution → HYDROSPHERE: 93 % of global ^{14}C**



Radiocarbon age determination

- sample radioactivity, A: number of decays per unit time (with N the number of ^{14}C atoms)

$$A = -\frac{dN}{dt} = \lambda N$$

- radiocarbon age then determined by integration and considering either the concentration N or the radioactivity A:

$$N = N_0 * \exp(-\lambda t) \rightarrow t = -\tau * \ln\left(\frac{N}{N_0}\right) \quad or \quad A = A_0 * \exp(-\lambda t) \rightarrow t = -\tau * \ln\left(\frac{A}{A_0}\right)$$

radiocarbon age ≠ calibrated radiocarbon or calendar age

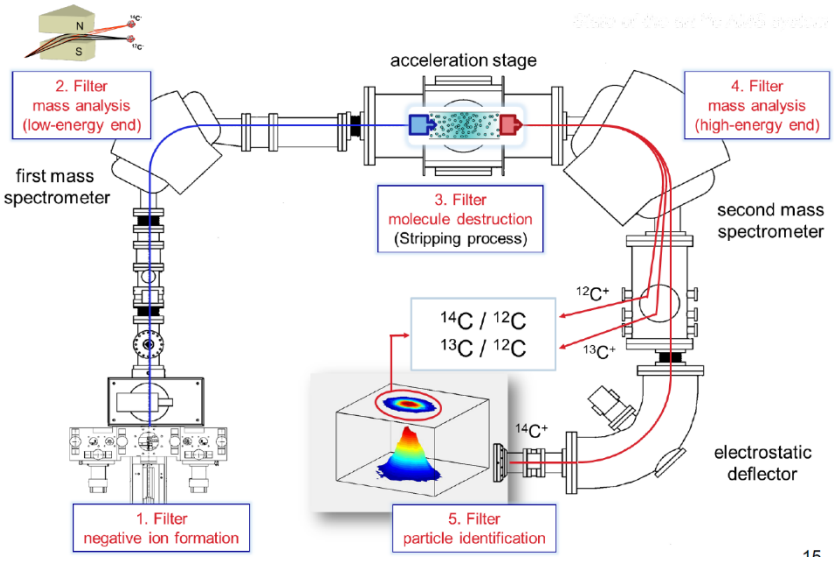
mainly because N_0 or A_0 is not constant

Methods of ^{14}C measurement

- $^{14}_{6}C \rightarrow {}^{14}_{7}N + e^- + \nu_e$ (^{14}C decays back to ^{14}N + e^-)
- **conventional method**:
  - determine ^{14}C activity of a weighted sample by counting the number of electrons emitted from nucleus per unit time by the decay of ^{14}C using a kind of modified Geiger counter
- **liquid scintillation counting**:
  - use of some organic solvents like benzene fluoresce when exposed to ionisation
  - let sample CO_2 react with molten Li to form Li_2C_2 which is hydrolysed to acetylene (C_2H_2) and trimerised to benzene (C_6H_6)
  - the benzene sample then counted by spectrometry (photomultipliers)
  - 1 g of average carbon: about 14 disintegrations per minute, therefore use more than 1 g and count for a long period (days)
- **accelerator mass spectrometry**:
  - directly determine the $^{14}C/^{12}C$ or $^{14}C/^{13}C$ ratio (ions are separated according to their mass/charge, m/e)
  - more efficient and sensitive than counting methods, typical measurement time ~30 mins
  - sensitivity: ca. 6 * 10^{-16} (lowest $^{14}C/^{12}C$ ratio measurable) ≡ 60,000 years ≡ 10 half-lives

Accelerator Mass Spectrometer (AMS)

- derived from nuclear physics instruments in the 60s and 70s
- should be able to remove any possible interference on mass 14 (^{14}N, $^{12}CH_2$, ^{13}CH) that are orders of magnitude more abundant than ^{14}C
- negative ion source at the beginning: $^{14}C^-$ passes, nitrogen cannot be negatively charged
- in the tandem accelerator, molecules become unstable & fall apart → you strip them apart
- subsequent filters follow which remove impurities
- instead of steering flow with lenses (as in a camera) you steer with magnetic fields
- the output is a ratio of $^{14}C/^{12}C$ which remains behind after the 4th filter



- measurements are typically made on graphite (CO_2 also possible)
- graphite formed by combustion of sample to CO_2 and then reduction of CO_2
- sample size < 1 mg C

Radiocarbon systematics

- AMS measurements yield a ratio $^{14}C/^{12}C$ → this ratio needs to undergo processing before being converted to a radiocarbon age
- fractionation effects occur when carbon is transferred from one pool to another → i.e. plants fractionate in respect to their habitats
- fractionation effects also occurs for ^{14}C that is incorporated differently compared to ^{12}C and ^{13}C in the different carbon pools
- the $^{14}C/^{12}C$ ratio is therefore dependent not only on age but also on the nature of the sample

  needs to be corrected for: normalization to $\delta^{13}C$ = -25 ‰

  the mean age correction is about 16 years for every 1 ‰ difference from – 25 ‰
- this way, we can take two samples with different fractionation rates & come up with the correct age fractionation (marine ^{14}C & plant ^{14}C may show different radioactive ages)
- AMS radiocarbon data commonly reported as:

- fraction of modern: **F**, **F_m**, **f_m** or Fraction Modern **$F^{14}C$**
- percent modern carbon: **pMC**

- the absolute international standard of ^{14}C activity is defined as 95 % of the ^{14}C activity of the original oxalic acid standard (HOxI), in the year 1950
- this is equivalent to the activity of 19th century (1890 AD) wood
- this value represents the ^{14}C concentration of the atmosphere prior to anthropogenic influence (i.e. fossil fuel combustion, atomic weapon testing, etc.)
- the measured activity of HOxI then first corrected for **fractionation effects** and also for radioactive **decay** between **1950 and the year of measurement**

- when a radiocarbon age (year date) is not desired, data often reported as $\Delta^{14}C$

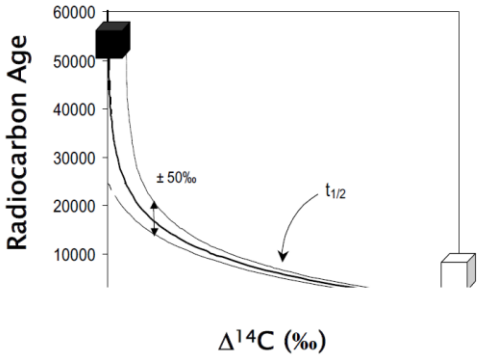
a) for samples with no age correction:

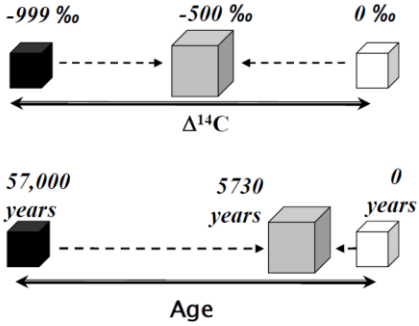
$$\Delta^{14}C = \left(\frac{A_{SN}}{A_{abs}} - 1\right) \cdot 1000‰$$

b) for samples with formation and measurement age: age correction
(y = year of measurement; x = year of formation or growth)

$$\Delta = \left(\frac{A_{SN} \cdot e^{\lambda(y-x)}}{A_{abs}} - 1\right) \cdot 1000‰ = \left(\frac{A_{SN} \cdot e^{\lambda(1950-x)}}{A_{ON}} - 1\right) \cdot 1000‰$$

- $\Delta^{14}C$ is useful for isotopic mass balance calculations
- black box: all ^{14}C still within the sample
- grey box: half-life occurred

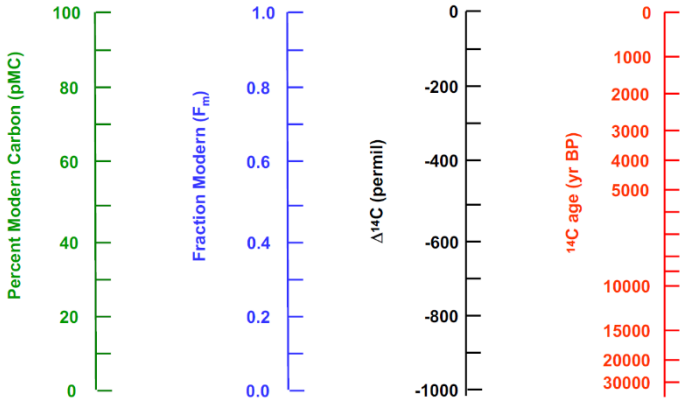




Reporting of radiocarbon data

- Fm and pMC report the fractional amount of ^{14}C in a sample relative to that in the standard
- a radiocarbon age (^{14}C yr) is not a calendar or chronological age and must be calibrated
- $\Delta^{14}C$ normalizes the ^{14}C content of a sample to the same $\delta^{13}C$ (-25 ‰) and time-point (1950 AD) → it is a linear quantity and can be used in mass balances

Factors controlling isotopic contents

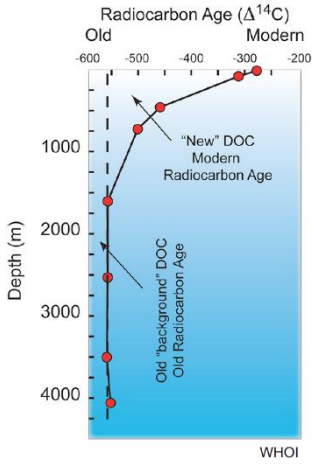


^{13}C	^{14}C
1. the carbon source utilized	1. the carbon source utilized
2. isotope effect of assimilation	2. n/a
3. isotope effect of biosynthesis	3. n/a
4. cellular carbon budget	4. n/a
5. n/a	5. Time

6. heterogeneity of sources	6. heterogeneity of sources

Factors influencing radiocarbon abundances

1. **Atmospheric ^{14}C variations**
   - variations in solar (cosmic ray flux) activity → long-term
   - variations in Earth's geomagnetic field strength → short-term
   - climate induced variations – solubility of CO_2 in water a function of temperature → a lot of ^{14}C dissolved in hydrosphere (see above: 93 % of global ^{14}C)
   - volcanic activity (outgassing of CO_2)
   - anthropogenic activity
     - fossil fuel burning
     - nuclear weapons test
2. **Source of "reservoir" effect**
   - there is rapid global mixing between atm. & terrestrial biosphere
   - however, mixing rates of deep ocean slow → mixing between surface mixed layer (high ^{14}C) and deeper layers (lower ^{14}C) gives rise to offset between mixed layer and atmosphere
   - this offset: ~400 years but varies spatially and temporally → thus organic matter in the oceans will have an **apparent age** which is 400 years older than terrestrial biomass synthesized at the same time

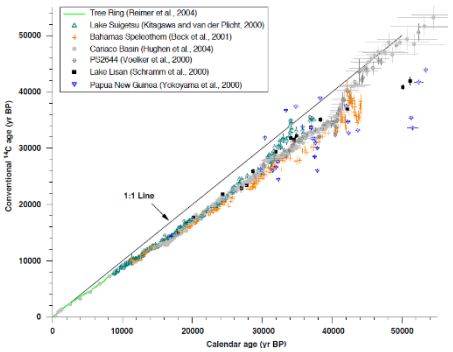


^{14}C variations and radiocarbon calibration

- changes in radiocarbon abundances can be used to track carbon cycling between pools
- past variations in ^{14}C, N_0 or A_0 need also be constrained to calibrate radiocarbon ages

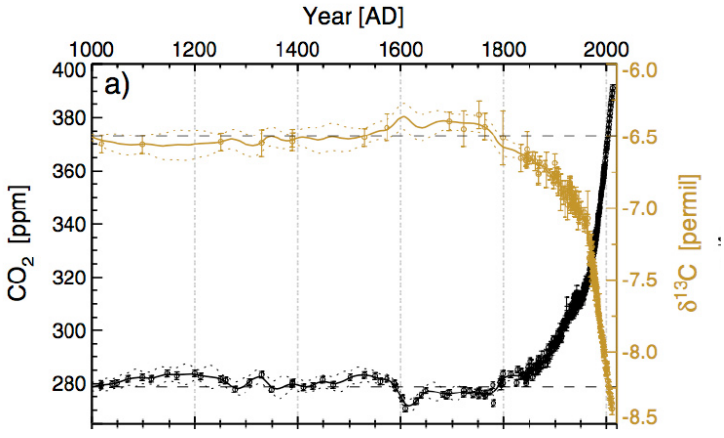
$$A = A_0 * \exp(-\lambda t), \qquad N = N_0 * \exp(-\lambda t)$$

- measure the radiocarbon content of objects of known age: e.g. tree rings or warves, etc.
- **dendrochronology**: matching ring width to obtain a long-term tree ring chronology on which ^{14}C measurements can be done
- global radiocarbon calibration dataset → infer calendar age from conventional ^{14}C age, relation not strictly 1:1 since c(^{14}C) in atmosphere changes over time due to anthropogenic influence



Potential limitations in assigning calendar ages from ^{14}C data

- we have uncertainties from the radiocarbon age determination and uncertainties in the calibrated date
  → **several possible dates & dating uncertainty**
- furthermore, the 1:1 ratio varies on short- and long-term scales
  - short-term: variations due to geomagnetic field changes
  - long-term: variations due to cosmic ray flux changes



^{14}C variations due to anthropogenic influence

- fossil fuel rich in ^{12}C (from organic reservoirs) → $\delta^{13}C$ goes down since ^{13}C gets diluted
- overall pCO_2 increases due to emissions since the industrial time
- at the same time [^{14}C] decreases due to overall more carbon in the atmosphere
- "bomb spike", peak in ^{14}C concentration in the 1960s due to nuclear bomb tests

→ this signal can be used to trace ^{14}C in the ocean & other carbon pools

4

Definitions:

- "A molecule those **carbon skeleton** can unambiguously be linked to that of a known biological precursor compound"
- more generally: "Organic compounds found in sediments which have properties that can be directly related to a known biological precursor"
- biological marker molecules are those biosynthesized by living organisms, they create a very small subset of the billions of molecules that can theoretically be assembled from C, H, O, N, S, P etc.

Molecular characteristics of biomarkers

- high degree of order in their molecular structure
- structural uniqueness → molecular structure (carbon skeleton), stereochemistry
  → example: only three C_{31} hydrocarbons have been identified in plants (normal-, iso-, and anteiso-) although there are > 10^9 possible isomers
- distributional uniqueness
  - isotopic composition (^{13}C, D/H)
  - abundance

Methane, CH_4 – the smallest biomarker?

- can potentially have isotopes of carbon (^{12}C, ^{13}C, ^{14}C) and isotopes of hydrogen (^{1}H, ^{2}H, ^{3}H)

DNA – the biggest biomarker?

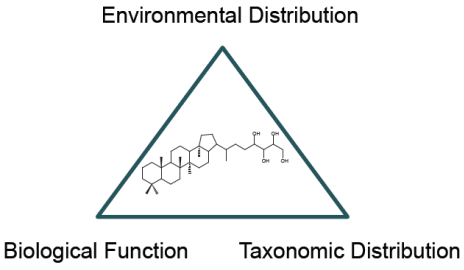
- consists of H, O, N, C, P and is made up of double-helix containing four types of molecules
  - Thymin = Adenin (double bond)
  - Cytosin ≡ Guanin (triple bond)
- DNA as a fragile molecule since sites are susceptible to
  - hydrolytic attack → can split C-N bonds
  - oxidative damage → can split double bonds
  - alkylation damage → can alter N atoms
  - condensation → can remove NH_2
- how good is DNA as a biomarker? really good but it is not preserved well, except for when it is in amber
- we need information richness in preservation

Key biomarker criteria:

- information content
- robustness of molecule
- ease of detection and analysis (both structural and isotopic)

Significance of biomarkers in the geologic record

- often compound made due to changes in the env. (e.g. ↑T ≙ more compounds are made)
- biological function: what for is it made?
- taxonomic distribution: by whom is it made?
- environmental distribution: why is it made?



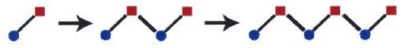
Lipids

- the cellular membrane lipids: a key source of information preserved in the rock record
- occur as "free" compounds or chemically bound (ester or ether linkages) to other biochemical components (e.g. glycerol)
- lipids present in the water column and in sediments can originate from all three domains of life (i.e. eukaryotes, bacteria, archaea)
- occurrence:
  - ubiquitous → german: allgegenwärtig, omnipräsent
  - 10 – 20 % of TOC in most organisms
  - extensively studied classes of compounds since they are
    - analytically accessible
    - diagenetically and chemically [relatively] stable
    - structurally extremely diverse (high potential as "biomarkers")
- functions:
  - long-term energy storage, membrane fluidity/rigidity regulators, membrane permeability, barrier to proton exchange, pigments, hormones, vitamins, anti-oxidant
- structure (tend to be hydrophobic due to long carbon chains):
  - fatty acids → COOH

  - fatty alcohols → OH
  - hydrocarbons
  - terpenoids
- fall into two main groups:
  - polyketide lipids
  - polyisoprene lipids

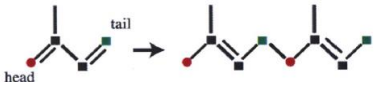
Lipid biosynthesis occurs via two main pathways

- **Polyketide Biosynthesis** → the polymerization of acetate (CH_3COOH) products typically have even carbon numbers



→ round ≙ CH_3, cubic ≙ COOH

- **Isoprenoid Biosynthesis** → the polymerization of isoprene ($CH_2=C(CH_3)CH=CH_2$) products typically have 10, 15, 20, ... carbon atoms



Polyketide lipids – long-chained ketons, esters

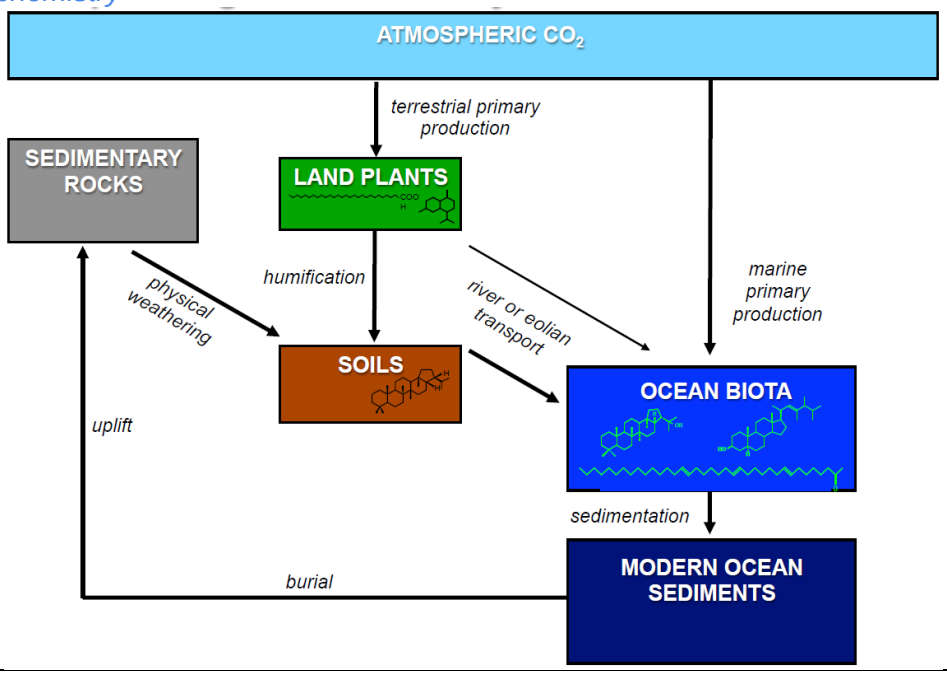
- long-chain unsaturated ketones (alkenones) have been identified in several species, especially the widely distributed coccolithophorids *Emiliania huxleyi*
- these compounds will be the focus of a different lecture
  - basically it's a 37C chain with either three or two double bonds: 37:3 or 37:2

Tetraterpenoids (C40)

- function as membrane rigidifiers
- again these compounds will be the focus of another lecture
- occur universally in all photosynthetic organisms
- some tetraterpenoids are the building blocks for carotenoid pigments (i.e. light absorbers)
  - having additional pigments helps with photosynthesis → being able to absorb more light or different light spectra than other phytoplankton species

Chlorophylls

- also occur universally in all photosynthetic organisms
- ancient analogue: porphyrins were the first molecules to be recognized in ancient sediments and petroleum as of biological origin – structurally related to chlorophylls → *this was seen as the beginning of organic geochemistry*



5a

- building blocks of organic matter
  - biochemicals (before sedimentation) consist of ~80 % of biopolymers and ~20 % lipids
  - sedimentary organic matter consist of ~50 % uncharacterized matter with ~40 % biopolymers and ~10 % lipids
  - uncharacterized OM cannot be used since it is not possible to trace back its origin
  - lipids however are relatively resistant and survive well in the records

Analytical Methods of extraction and separation

(1) bulk measurements

- optical assessment (identification of spores, pollen, algae, higher plant debris, etc.)
- elemental analysis (C, H, N, O, S)
- isotopic analysis ($\delta^{13}C$, $\delta^{15}N$, δD, $\delta^{34}S$, $\Delta^{14}C$) of bulk matter
- advantage: fast, easy, minimal preparation and no fractionation of the sample
- disadvantage: low information content and insensitive to subtle chemical variations

(2) molecular-level measurements

- advantage: high biological information content, can often characterize and quantify more than one molecular type
- disadvantage: slow → often complex, very complex mixtures encountered – often can't identify all compounds isolated and accurate quantification challenging

Sample storage and preparation for organic geochemical analysis

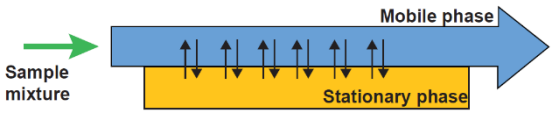
- **Sample Storage**
  - many organic compounds are biologically or chemically labile
    - susceptible to hydrolysis (e.g. DNA), photolysis (e.g. certain hydrocarbons) or oxidation (e.g. unsaturated lipids)
  - ideally samples should be frozen in the dark and under N_2 atmosphere
    - sometimes, a fridge is also enough to stabilize compounds for a short while
- **Sample Preparation**
  - drying of samples will deactivate enzymes, but can lead to oxidation of selected compounds
  - options: air-dry, freeze-dry or extract wet
- **Practical considerations**
  - potential contamination sources → glass, teflon, aluminium foil, stainless steel
  - materials to avoid → parafilm, polystyrene, silicone grease (use gloves to protect sample)
  - cleaning of reagents/labware → combustion at 450 degrees, use sulfuric acids or certain detergents as well as solvent rinsing (Dichlormethane, Methanol)
- **Solvents**
  - important in extraction of compounds of interest from a biological or env. matrix and for chemical modifications of compounds to facilitate separation
  - good solvent should have: polarity, a low boiling point (makes its removal later easier), inertness (should not take part in chemical reactions)

Lipid extraction methods

- **Ultrasonic extraction** → using vibrations to disrupt sample in solvent
  - advantage: quick and a sequence of solvents may be used
  - disadvantage: physically violent process which may cause breakdown of macromolecules and clay
- **Accelerated Solvent Extraction (ASE)** → more automated version of the previous example, this time extraction elevated at 100℃ and 1000 psi
  - advantage: quick, low solvent consumption, automated
  - disadvantage: may not be appropriate for thermally labile compounds and it's expensive
- **Microwave-assisted extraction**
  - advantage: quick, moderate solvent consumption, automated, can process large samples
  - disadvantage: may not be appropriate for thermally labile compounds, expensive and requires separation of extract from residue

Chromatographic Separation, Purification and Analysis

- definition of chromatography: “the resolution of material on two phases using chromatographic apparatus”
- chromatography uses two phases: one of which is stationary and the other mobile
  - use of different physical properties to induce separation of compounds and compound classes



The molecules of the mixture interact with the molecules of the mobile and stationary phase → Retardation of the movement of molecules

Different types of molecules interact differently with MP and SP → The total retention time of molecules is variable depending on molecules: **separation**

Column (Gravity) Chromatography (CC)

- advantage: can perform large-scale separations (several hundreds of milligrams of solute)
- disadvantage: lower resolution than THC or HPLC (see below) and separation is generally performed ‘blind’
- methodology:
  1) mixture to be separated is dissolved in the mobile phase in the vertical tube
  2) mobile phase is added throughout the process
  3) components sink to the bottom, some are faster than others and each compounds is collected as it reaches the bottom

High Performance Liquid Chromatographer (HPLC)

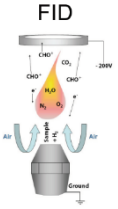
- relies on pumps to pass a pressurized liquid solvent containing the sample mixture through a column filled with a solid adsorbent material
- each component of the sample interacts slightly different with the adsorbent material → causing different flow rates of the different compounds and thus leading to separation as the flow out the column

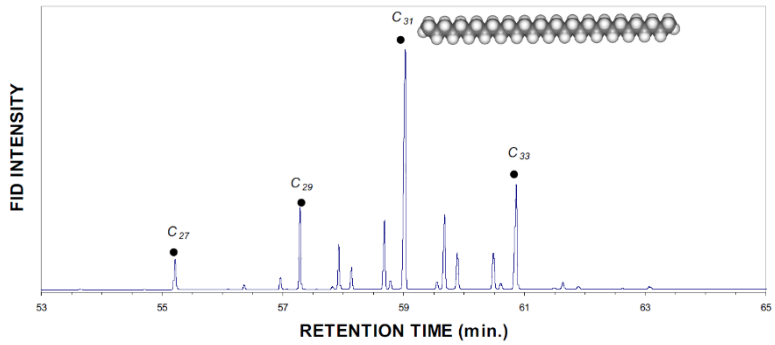
Gas Chromatography (GC)

- sample and solvent transferred as gas, most commonly used
- e.g. what the PhD student at Uni Bern did: burning of tree ring carbon and detection of carbon in it
- gas supplies
  - carrier gas (e.g. H_2, He)
  - detector gases
- oven (typical temperature program 50°C - 320°C at 4°C/min
- GC column characteristics
  - liquid stationary phase as the outer layer: must be non-volatile, thermally stable, not react with solute

Detection and identification of compounds

- the detection of compounds after separation depends on the phase (liquid vs. gas) and the compounds themselves
- the chromatographic detector is capable of establishing both the identity and concentration of eluting components in the mobile phase stream
- **Liquids** (e.g. HPLC)
  - light absorption at specific frequency: magnitude of absorption = f(concentration)
  - fluorescence
  - mass spectrometry
- **Gases** (e.g. GC)
  - flame ionization detector (**FID**): ionizes organic compounds in H_2 flame and generated current is measured on the anode (only organic, destructive)
  - thermal conductivity detector (TCD): measures change in conductivity relative to a reference flow
  - mass spectrometry: charged molecules separated on the bases of mass to charge ratio → high sensitivity and selectivity





Example gas chromatogram of plant waxes (alkane fraction) from Tobacco leaves

- FID scan in time
- very abundant uneven chain lengths → more generally the case in land plants
- the chain-length distribution of these compounds is indicative of growth temperature

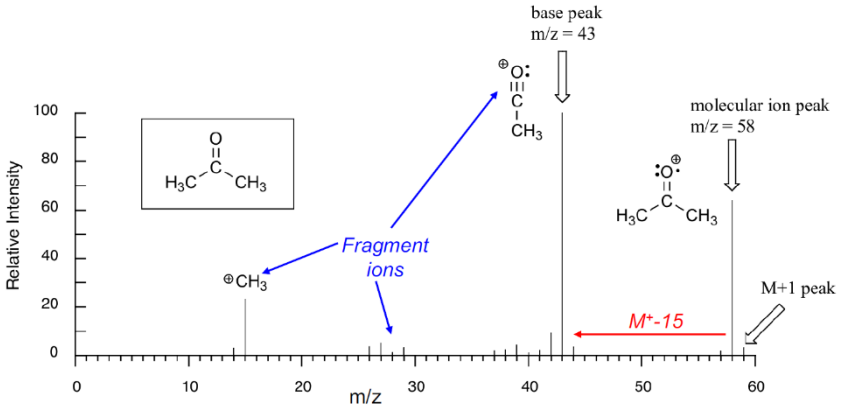
General operation

1. create gas-phase ions
2. separate the ions in space or time based on their mass-charge ratio
3. measure the quantity of ions of each mass/charge ratio

→ since MS systems create and manipulate gas-phase ions, they operate under high vacuum

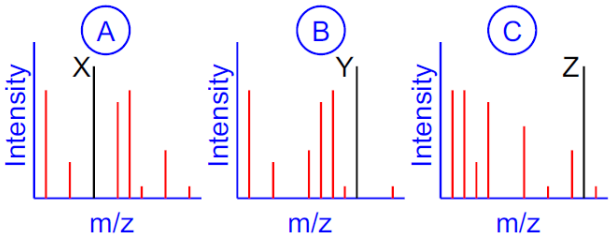
Mass Spectrometry

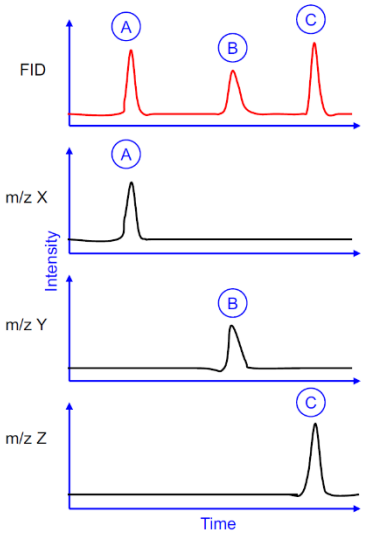
- Important features of mass spectra
  - molecular ion (M^+): intensity will depend on stability of molecular structure and ease of fragmentation
  - base peak (B^+): may be molecular ion or favored fragment ion, depending on structure
  - fragment ions: may be formed by cleavage, loss of neutral fragments or by structural rearrangement (may be many or few)



- the mass spectrum of acetone (CH_3COCH_3) contains fragment ions as well as the molecular ion at m/z = 58
- from one molecule you get multiple peaks, most abundant peak at 43
- the bigger the molecule, the less stable they are
- major influences on mass spectral fragmentations of organic compounds:

1. ring structures
2. branching points
3. double bonds
4. aromaticity
5. stereochemistry
6. functionality





Example:

- mass spectra are collected for unrelated compounds A, B and C separated from a mixture by GC and the FID method (burn the sample)
- mass x, y and z are found to be uniquely characteristic for compounds A, B and C respectively
- can perform mass chromatography using diagnostic ions

Week 5b – Stable Isotopes in Organic Geochemistry

5b

stable isotopes of hydrogen

ISOTOPE	ABUNDANCE
^{1}H	99.98 %
^{2}H or D	0.02 %
^{3}H or T (very rare)	natural levels very low

- ratio D/H = $2 * 10^{-3}$ on average
- standard reference material
  - Standard Mean Ocean Water → SMOW which has D/H of $1.5576 * 10^{-3}$

stable isotopes of carbon

ISOTOPE	ABUNDANCE
^{12}C	98.89 %
^{13}C	1.11 %

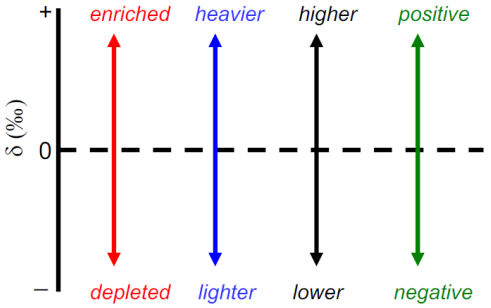
- ratio $^{13}C/^{12}C = 1.225 * 10^{-2}$ (on average)
- however, this ratio varies slightly among different carbonaceous materials
- standard reference material:
  - PeeDee Belemnite (carbonate) → PDB which has a $^{13}C/^{12}C = 1.123 * 10^{-2}$

Stable carbon isotopes

- Notation and nomenclature

$$\delta^{13}C_{sample} = \left(\frac{^{13}C/^{12}C_{sample}}{^{13}C/^{12}C_{standard}} - 1 \right) \times 1000$$

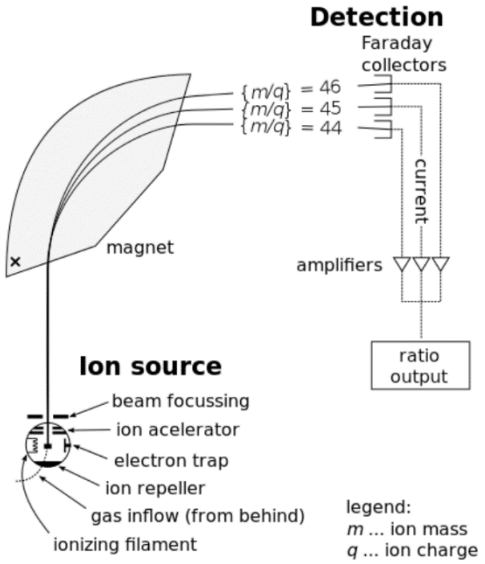
- positive values (more ^{13}C) = 'enriched', 'heavier', 'higher'
- negative values (more ^{12}C) = 'depleted', 'lighter', 'lower



→ other stable isotopes (O, N, S, ...) less abundant in organic compounds & may be measured in extremely rare cases

Isotope ratio mass spectrometry (IRMS)

- principle:
  - magnetic sector instrument (no scanning)
  - isotope ratios can be precisely measured using a sector mass spectrometer
  - the MS precisely measures the ratio of currents from ion beams corresponding to different isotopes (e.g. for $^{13}C/^{12}C$, measure $^{13}CO_2^+$ (m/e = 45) and $^{12}CO_2^+$ (m/e = 44)
  - ratio is compared to a standard reference gas
- conventional method:
  - introduction of gases via dual viscous inlet

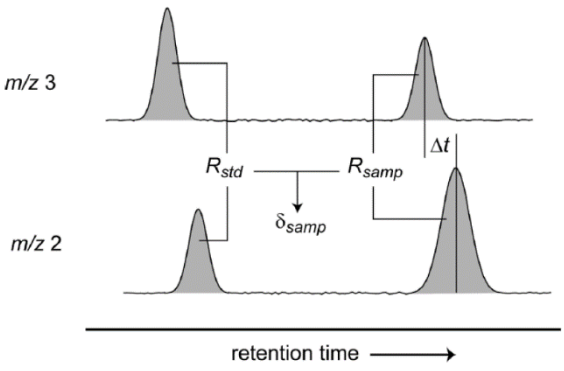


- introduce sample in the beginning, e.g. CO_2
- an electric impact ion source generates positive ions that are mass analyzed by a single magnetic sector
- ions after ion source are accelerated
- according to mass, the ions get reflected at a certain rate which results in differing paths out of the magnetic field

M44: $^{12}C^{16}O^{16}O$

M45: $^{13}C^{16}O^{16}O$ ($^{12}C^{17}O^{16}O$) → very rare

M46: $^{12}C^{18}O^{16}O$



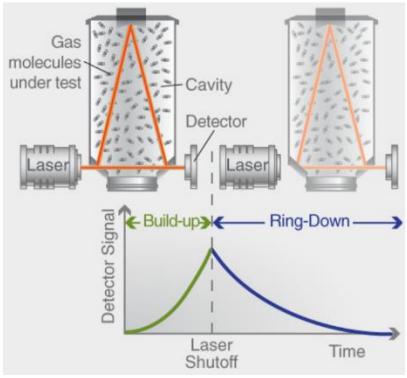
Isotope ratio monitoring analysis → Figure to the right

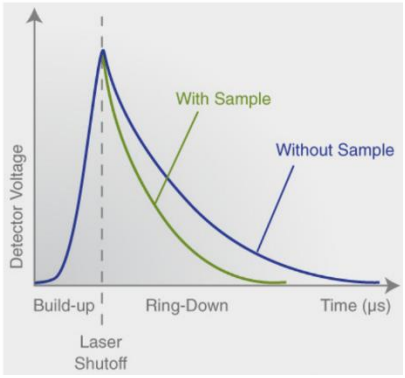
- two or more ion currents (here masses 2 and 3, corresponding to H_2^+ and HD^+) are measured simultaneously by multiple Faraday detectors
- peak areas then computed taking into account the time shift due to isotope chromatography (Δt_r, greatly exaggerated in this figure for clarity)
- peak areas then compared to compute the ion-current ratio (R) for each analyte

- finally, ion-current ratios are compared between sample and standard to calculate the delta value (here δD) of the sample
- in a typical analysis, the sample is compared to two or more isotopic standards

Cavity Ring-Down Spectroscopy (CRDS)

- much faster and more fancy
- since ~5 years at many labs now
- light travels via mirrors from laser to detector via mirrors
- very small part of light gets absorbed by the molecules and modifies frequency of the light detected
- different isotopes have different absorption spectra and this way the isotope ratio can be inferred





Processes controlling isotope composition of oceanic and sedimentary organic matter

- **Production**
  - primary production → photosynthesis – phytoplankton, higher plants, cyanobacteria
  - secondary production → chemoautotrophy – sulfide oxidizers, ammonia oxidizers, methanogens, fermentation
- **Recycling**
  - aerobic recycling → respiration – aerobic heterotrophic bacteria, methane recapture – methanotrophs

Isotope fractionation

- an isotope effect (a physical phenomenon) leads to fractionation (an observable quantity)
- the magnitude of the isotope effect is expressed as a fractionation factor
  - e.g. for equilibrium isotope effect:

$$^{13}CO_2(g) + H^{12}CO_3^-(aq) = {}^{12}CO_2(g) + H^{13}CO_3^-(aq)$$

- fractionation factor α as a very complicated ratio
- a related expression is the “difference fractionation factor”

$$\varepsilon \equiv \Delta^{13}C = \delta^{13}C_{product} - \delta^{13}C_{reactant}$$

- two types of isotope effect:
  (i) equilibrium isotope effects
  (ii) kinetic isotope effects

Equilibrium isotope effects

- the heavy isotope (^{13}C) is concentrated in the chemical compound in which it is bound most strongly → i.e. carbonic acid, $H_2CO_3(aq)$, and bicarbonate, HCO_3^- are enriched in ^{13}C relative to CO_2 in solution by ca. 8%
- **in equilibrium** isotope effects, the **difference** between the reactant and product **depends only on temperature**, and not the distribution of material between product and educt
  - e.g. while relative abundance of $CO_2(aq)$ and HCO_3^- varies as a function of pH, isotope differences only vary with temperature

Kinetic isotope effects

- kinetic isotope effects result from differences in conversion rates between ^{13}C and ^{12}C from reactant to a product (E_{act} for lighter isotope is smaller & thus will react faster)
- two processes which give rise to kinetic isotope effects:
  - transport processes
  - chemical processes
- normal = light isotopic species reacts more rapidly
- inverse = heavy isotopic species reacts more rapidly
- primary = isotopic substitution at a position to which a chemical bond is made or broken influences the reaction rate

- secondary = isotopic substitution at a remote position influences the reaction rate

Isotope fractionation during photosynthesis, ε_p

- in photosynthesis, $^{12}CO_2$ preferentially taken up relative to ^{13}C → two stages when kinetic isotope effects can occur:

1. **transport (diffusion) processes**

- gas phase diffusion (i.e. atm. CO_2 → dissolved CO_2 in leaf)
  - approx. fractionation factor: 4.4 permille (i.e. depletion = - 4.4 permille
- liquid phase diffusion of CO_2 or HCO_3^-
  - approx. fractionation factor: ~ 0.8 permille (relatively minor)

2. **chemical (enzymatic) processes**

- four photosynthetic pathways:
  i) C_3 → Calvin – Benson
  ii) C_4 → Hatch-Slack
  iii) and two minor ones

The C_3 Calvin – Benson photosynthesis

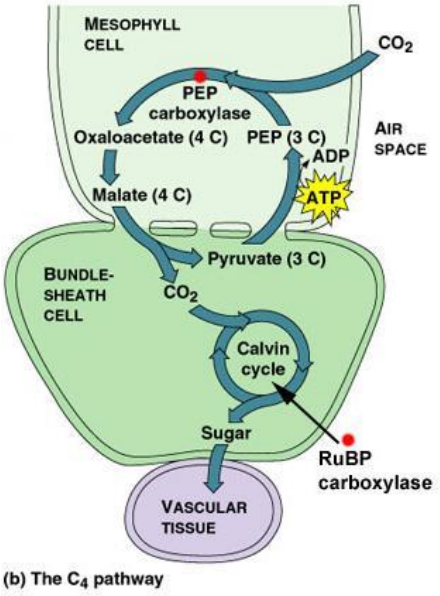
- common among terrestrial plants (e.g. trees) and phytoplankton/cyanobacteria
- about 85% of the plants are C_3 (including rice, wheat, soybeans and all trees)
- CO_2 fixation is catalysed by ribulose-1,5-biphosphate (RUBISCO) and with a series of intermediate steps converts it to sugars that can be used by the plant
- overall reaction:

$$6CO_2 + 12\,NADPH + 18\,ADP \rightarrow C_6H_{12}O_6 + 12\,NADP^+ + 18\,ADP + e^-$$

- if temperatures are too high, O_2 is preferentially fixed by RUBISCO and the plant enters photorespiration: loss of CO_2 with negative consequences for the plant
  - O_2 enters into the plant and CO_2 leaves → basically the opposite of what the plant actually wants

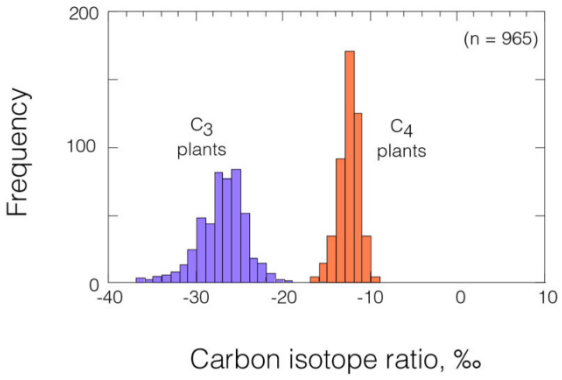
C_4 Hatch – Slack photosynthesis

- in C_4 plants, the light-dependent reactions and the Calvin cycle are physically separated → this minimizes photorespiration and these plants are better adapted to warm climates
- atm. CO_2 is fixed in the mesophyll cells and forms malate (4-C) through the PEP caboxylase enzyme
- malate then transported inside and releases CO_2 → this CO_2 then fixed by RUBISCO and made into sugars via the Calvin cycle exactly as in C_3 plants
- less common among terrestrial plants (e.g. sugar cane, corn and tropical grasses, desert plants, ...)



(b) The C_4 pathway

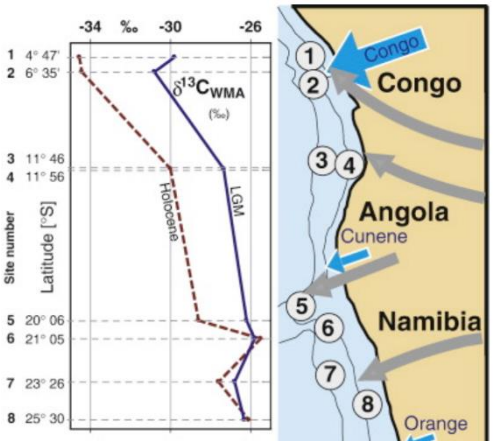
Contrasted C_3 and C_4 isotopic composition



- C_3 plants preferentially take up the lighter ^{12}C and have a more negative $\delta^{13}C$ signal
- rise of C_4 plants in the late Miocene (~ 7 Ma) due to changes in environmental and climate conditions: rainfall patterns/monsoon → drivers still debated
- in summary: the use of biomarkers together with the isotope ratio can refine the source of the signal (e.g. algae vs. land vegetation)

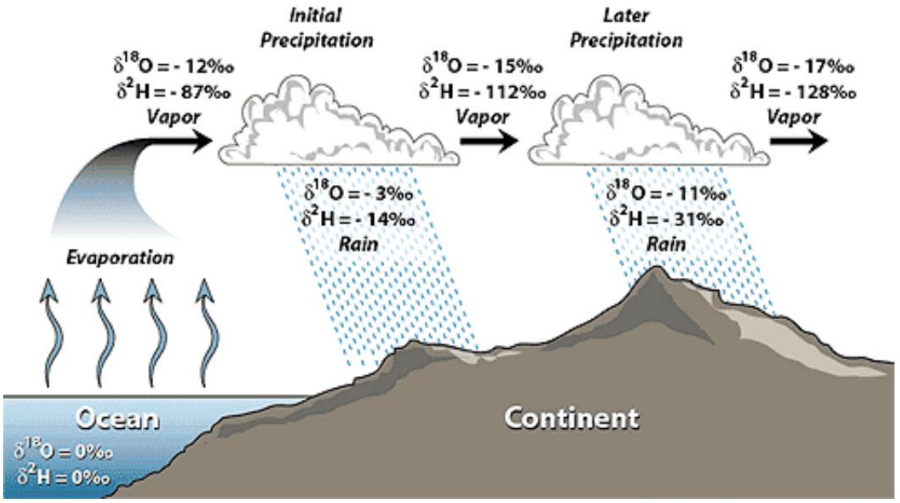
Compound specific carbon isotopic composition as maker of terrestrial vegetation changes → Eglinton & Eglinton, 2008

- slight difference between C_4 tropical grass on the continent and marine sediment isotopic ratios
- Eglinton & Eglinton analysed plant-wax lipids in ocean sediments
- several river systems flow into the eastern Atlantic and bring OM from the inner African continent
- slightly less negative values of $\delta^{13}C$ in marine sediments off the coast of central Africa during the last glacial maximum (LGM)
  - less precipitation was available
  - more arid conditions
  - more C_4 plants lived on the continent



Hydrogen isotopes in organic compounds (i.e. ^1H, ^2H or D)

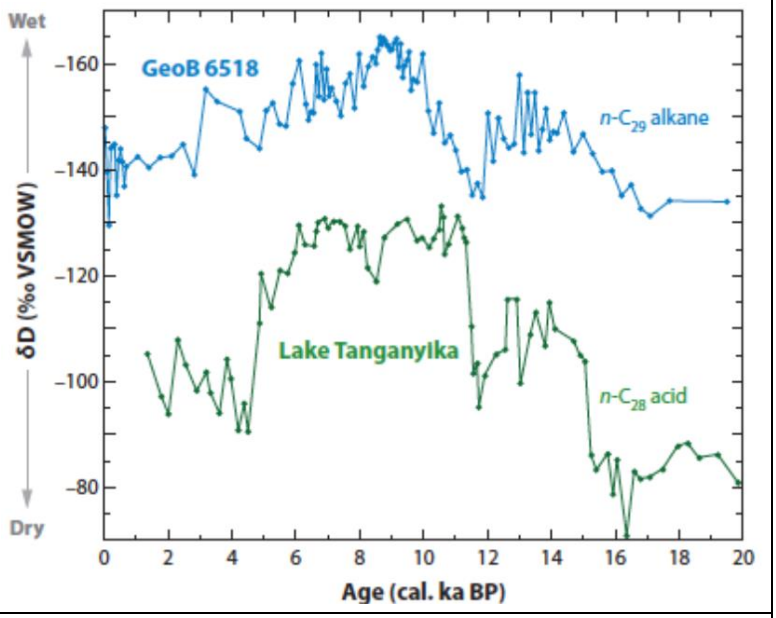
- hydrogen isotopes distribution at the Earth's surface is largely controlled by the water cycle
- as water vapor is longer in the air, the more and more depleted it gets in ^{18}O since the heavier isotope more likely rains out and the vapor shows a negative $\delta^{18}O$ signal
- ice sheets with a $\delta^{18}O$ signal of -33 to -55



http://web.sahra.arizona.edu/

Hydrogen isotopes in organic compounds have great potential for paleohydrology:

- distinction between wet and dry climate using δD deviations from the reference Vienna Standard Mean Ocean Water (VMSOW)
- the major influence on δD is the difference between ocean temperatures where the moisture evaporated and the place where the final precipitation occurred
- δD values get progressively more negative the higher latitude the precipitation occurs → same principle as $\delta^{18}O$
- the δD values reflect the level of rain-out from the air mass which correlates with temperature
- nevertheless, $\delta^{18}O$ remains the most robust and widely used proxy for past temperatures



Week 6 – The Oceanic Biological Pump

6

- biological pump allows transport between deep water, surface waters and the atmosphere
- key mechanism for removing CO_2 from the atmosphere and sequestering it in the deep ocean
- foundation of food chains and fisheries
- consists of
  - **solubility pump** → uptake and outgassing of CO_2
  - **organic carbon pump** → net CO_2 fixation from organic matter (marine or terrestrial)

- **carbonate pump** → dissolution and precipitation of $CaCO_3$ from (Ca, Mg)Silicates or from shells of marine organisms
- **microbial carbon pump** → DOC transport

Solubility pump

- cooler waters hold more DOC at equilibrium
- cooler waters more dense & form deep water masses → creates vertical gradient of DIC in the ocean
- air-sea heat fluxes drive air-sea carbon fluxes (i.e. when ocean loses heat during ENSO events carbon is taken up
- ocean gains carbon in North Atlantic Ocean (NADW formation) and Southern Ocean (AAIW) while it loses heat in equatorial regions (esp. eastern equatorial Pacific)
- ocean gains heat (on interannual time scales) in equatorial regions

- *$\downarrow T \triangleq \uparrow$solubility CO_2*
- *$c(DIC) > c(DIC)_{eq.}$ in the deep ocean*

Dissolved Inorganic Carbon
$DIC = [H_2CO_3^-] + [HCO_3^-] + [CO_3^{2-}]$

- DIC is conservative with respect to changes in pH, T, S and mixing

Distribution of carbon in the ocean as a combination of

1.) transport → relationship to salinity & density
2.) "solubility pump" → relationship to temperature (i.e. cooler waters ≙ higher CO_2 solubility)
   - deep water masses substantially enriched in DIC (i.e. NADW and NPDW)
   - DIC in the deep ocean exceeds the equilibrium concentration at that temperature due to the biological pump
3.) "biological pump" → relationship to PO_4^-

Biological 'soft-tissue' pump

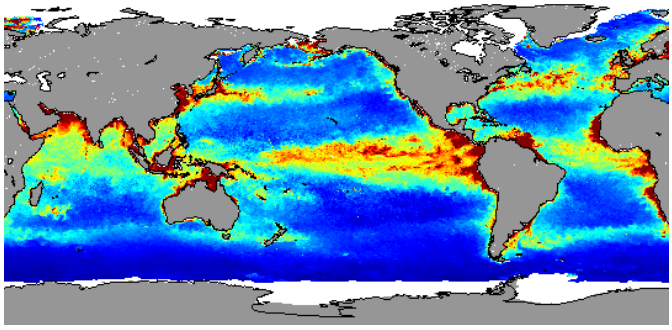
- *photosynthesis* → in the sunlight region, i.e. in the euphotic zone (upper ~150 m)

$$106CO_2 + 16NO_3 + H_2PO_4 + 122H_2O + hv \rightarrow C_{106}H_{263}O_{110}N_{16}P + 138O_2$$

- *respiration* → remineralization or organic matter which consumes oxygen
- *Redfield Ratio* → oceanic organic matter has a "fixed" ratio of carbon and nutrients
- strong similarity between DIC and PO_4 distribution in the ocean → remineralization of organic matter in the deep ocean and accumulation there
- mean primary production concentrated at continental upwelling regions
- gyres as deserts in mean primary production

Redfield concept of constant stoichiometric ratios

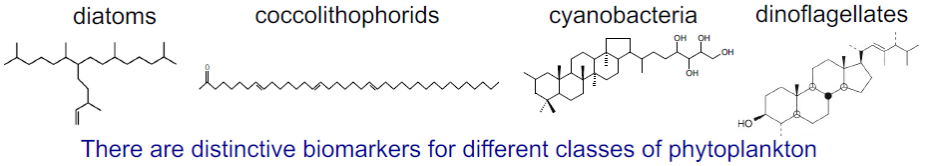
- *composition of organic matter $C:N:P:O_2 \approx 106: 16: 1: -150$*
- *remineralization below 400 m $C:N:P:O_2 \approx 117: 16: 1: -170$*
- *used to calculate biological production as a function of nitrogen or phosphorus*



Primary producers in the modern ocean

- main primary producers in the ocean (phytoplankton) are a diverse group of photoautotrophic organisms
- **diatoms** → produces SiO_2 shells
- **cocoolithophorides** → e.g. forams, produce $CaCO_3$ shells
- **cyanobacteria** → can fix N_2 and thus live in harder conditions
- **dinoflagellates** → can have inorganic and organic skeletons

→ there are distinctive biomarkers for different classes of phytoplankton



There are distinctive biomarkers for different classes of phytoplankton

Fate of exported organic matter

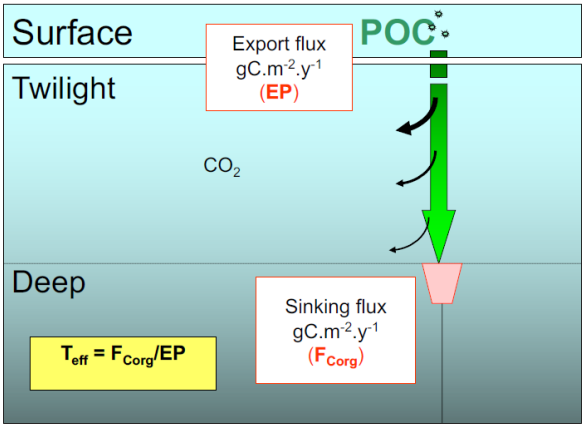
- most gets eaten by heterotrophs, such copepods (zooplankton) → these little guys can swim and follow food around
  - zooplankton hide during the day from fish in the deeper layers and feed during night
- left over material sinks → the larger the particle, the faster its transport
- fecal pellets and aggregates (i.e. marine snow) are most likely to sink deep

Some definitions

- **Export production (EP)** → amount of organic matter produced in the ocean by primary production that is not recycled (remineralized) before it sinks into the aphotic zone (~100 m)
  - measured in units of carbon, i.e. [mgC m^{-2} d^{-1}]
- **Transfer efficiency (T_{eff})** → flux of organic carbon (FC_{org}) divided by EP for a specific depth in the water column (e.g. 2000 m, ~M/B boundary)

Modes of vertical transport of POC in the pelagic ocean interior

1.) **gravitational transport** of POC by ballasted amorphous aggregates
2.) **passive transport** of POC by the zooplankton ecosystem
3.) **downward transport** of OC (POC and DOC) by **overturning**
4.) **terminal gravitational transport** of POC in the bathypelagic and abyssopelagic zone



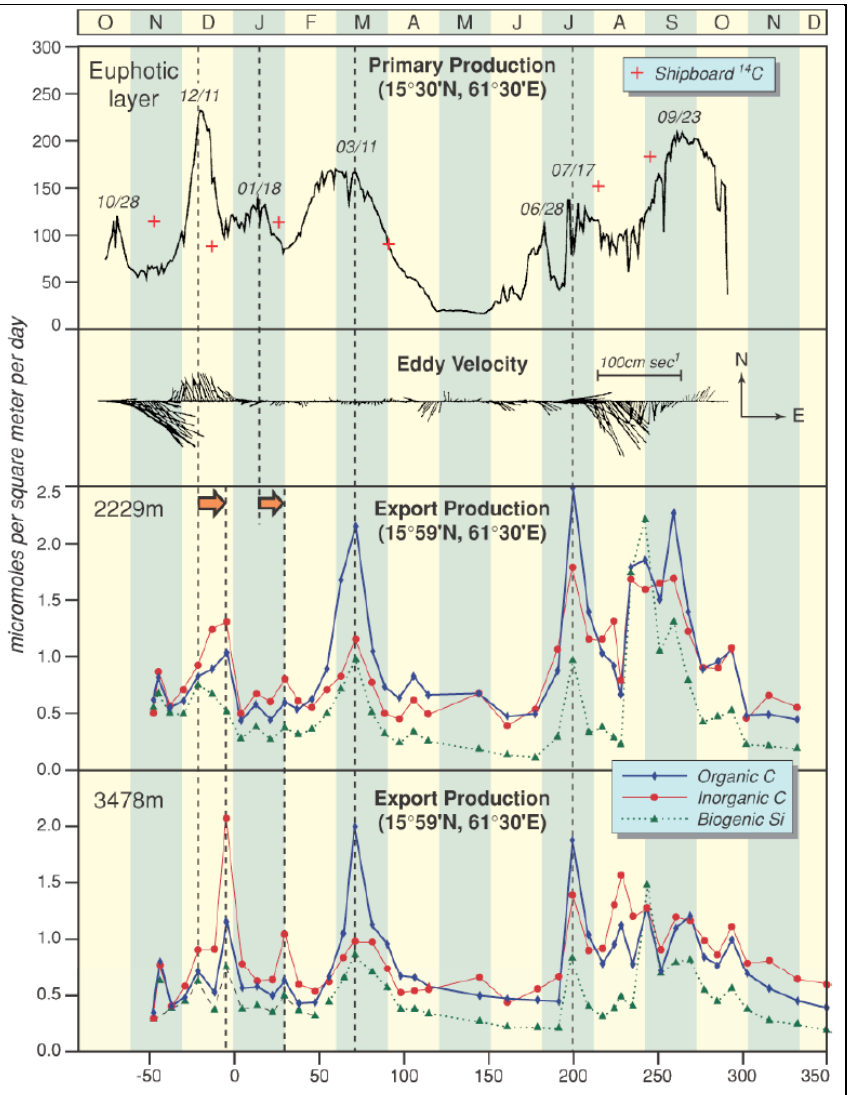
Universal biogeochemical elements

- **C_{org}:** particulate organic carbon: POC
- **C_{inorg}:** biogenic $CaCO_3$ carbon: PIC
- **Si_{bio}:** biogenic opal SiO_2 * nH_2O
  flux term: mol, $m^{-2}yr^{-1}$

Temporal evolution in biogenic flux

- flux measurements with sediment traps
  - cups collect material & biology → rotating cups fill each two weeks for an extended period of time
  - order of employment usually one year
  - disadvantage:
    - organic matter inside cups attract organisms which die due to poisonous substance and bias measurement signal
    - prone to bias especially when deployed in the mesopelagic zone (< 1000 m; "swimmer effect" or in areas of strong current velocity ("hydrodynamic effect")

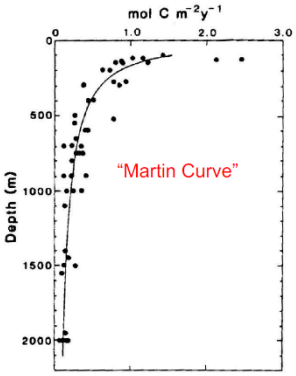
- offset between euphotic layer NPP estimate by satellites and EP in bathypelagic layer by sediment traps (OM needs time to sink)
  - can be used to measure flux
- + symbols in euphotic layer denote ^{14}C estimates
- clear peaks in NPP due to ideal T, light & nutrient conditions
  - spring bloom and fall bloom, in summer water stratified and nutrients remain below
- amplitude muted the deeper in the ocean



Martin et al (1987) equation

$$\frac{F_{C_{org}}}{EP} = \left(\frac{z}{100}\right)^{-0.858}$$

- global average T_{eff}: **0.08** (i.e. 8% of carbon leaves euphotic zone & sinks below 2000 m)
- transfer efficiency can vary substantially on local scales (e.g. in Japan higher flux than in Hawaii)

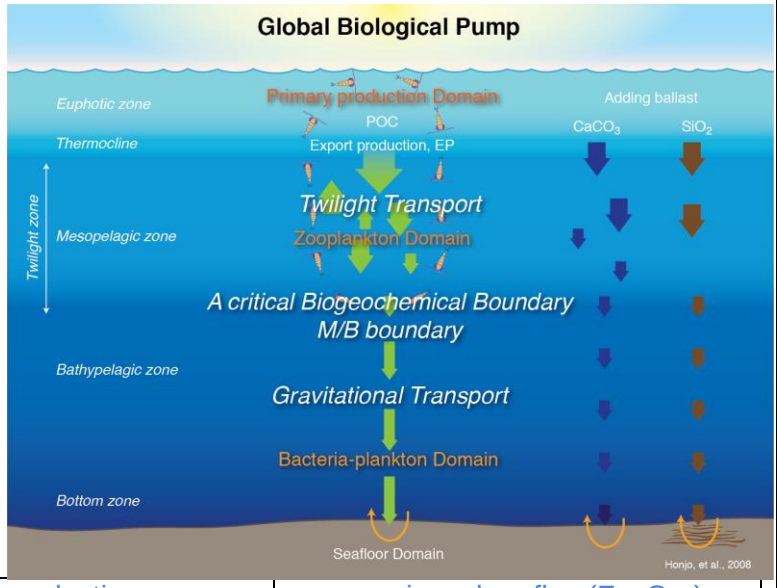


Factors controlling the flux of organic carbon to the bathypelagic zone of the ocean

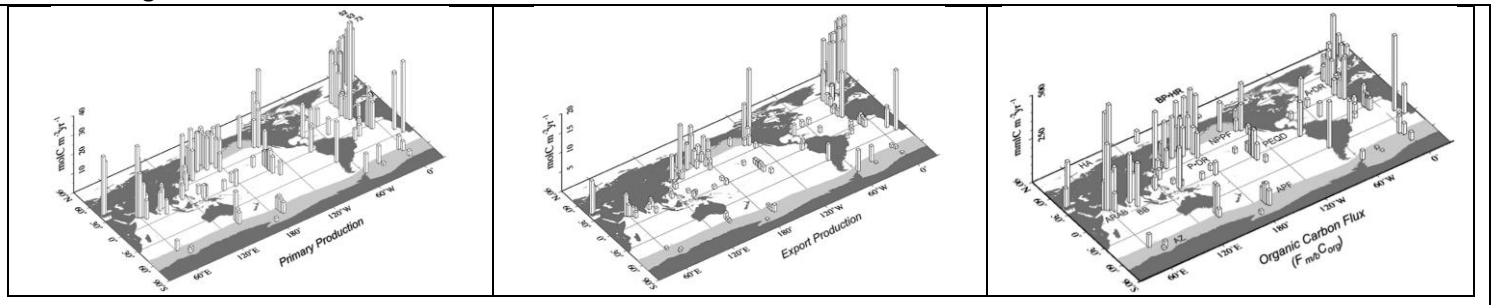
- *[...] The ballasting effect of biogenic minerals may be an important factor promoting export of organic carbon to the deep sea by increasing the density of settling particles. [...]* François et al., 2002
- they found positive correlation (i.e. $R^2 = 0.65$) between particle flux and carbonate flux magnitude → i.e. ↑$CaCO_3$ flux ≙ ↑F_{Corg}/EP
- dust, clay and other lithogenic material can also act as ballast to enhance sedimentary flux

Geographic variations in the transfer of carbon to the deep sea

- in general: photosynthesis needs
  - **light** (which varies with latitude and season)
  - **nutrients** (varies geographically)
- overall correlation on global surface nutrients concentration and chlorophyll-a concentration except in 'High-Nutrient-Low-Chlorophyll' HNLC regions such as the Southern Ocean or the subtropical gyres
  - low NPP due to downwelling/lack of trace nutrients such as Fe
- most marine primary production in the North Atlantic Ocean and North Pacific Ocean
- highest organic carbon fluxes also in those areas
- as well as export production



primary production	export production	organic carbon flux ($F_{m/b}C_{org}$)



Particulate organic carbon fluxes to the ocean interior
and factors controlling the biological pump: A synthesis
of global sediment trap programs since 1983

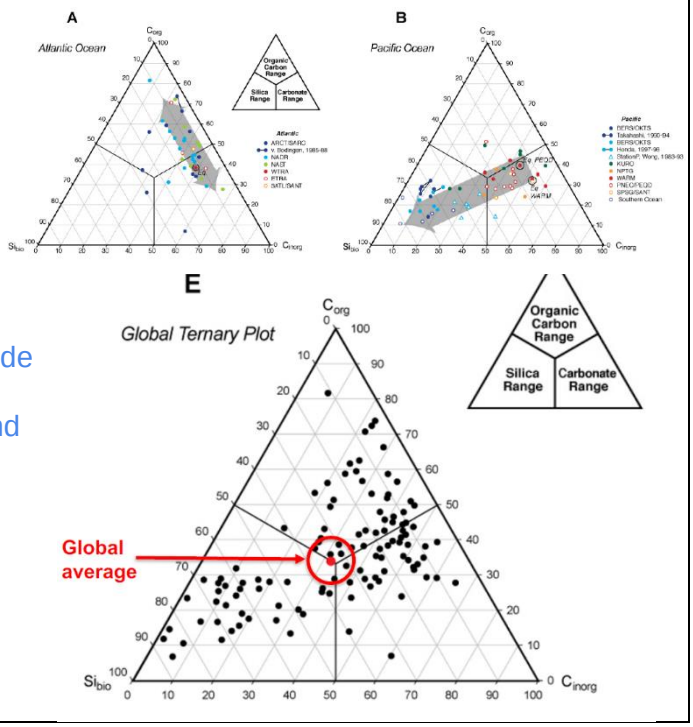
Susumu Honjo[a,*], Steven J. Manganini[a], Richard A. Krishfield[a], Roger Francois[b]

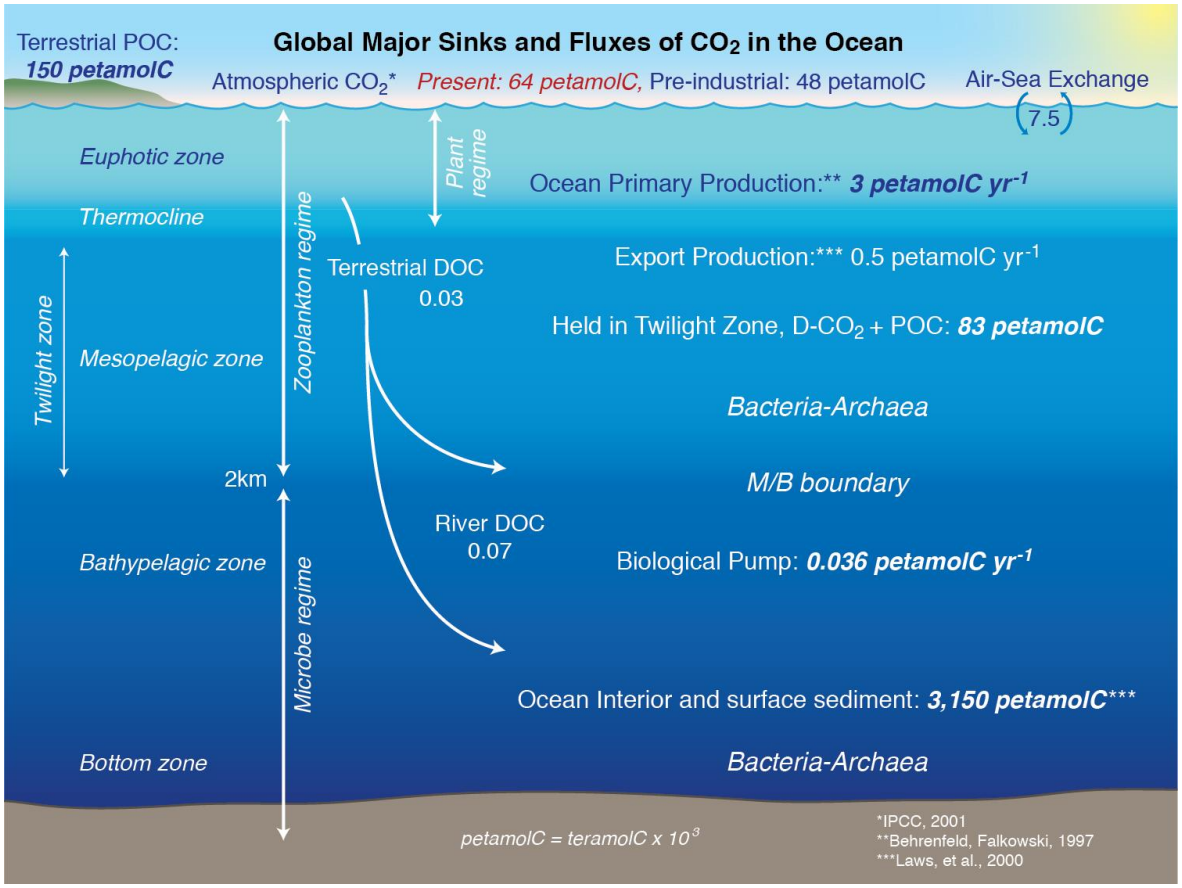
[a] *Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA*
[b] *Department of Earth and Ocean Sciences, University of British Columbia, Vancouver, Canada*

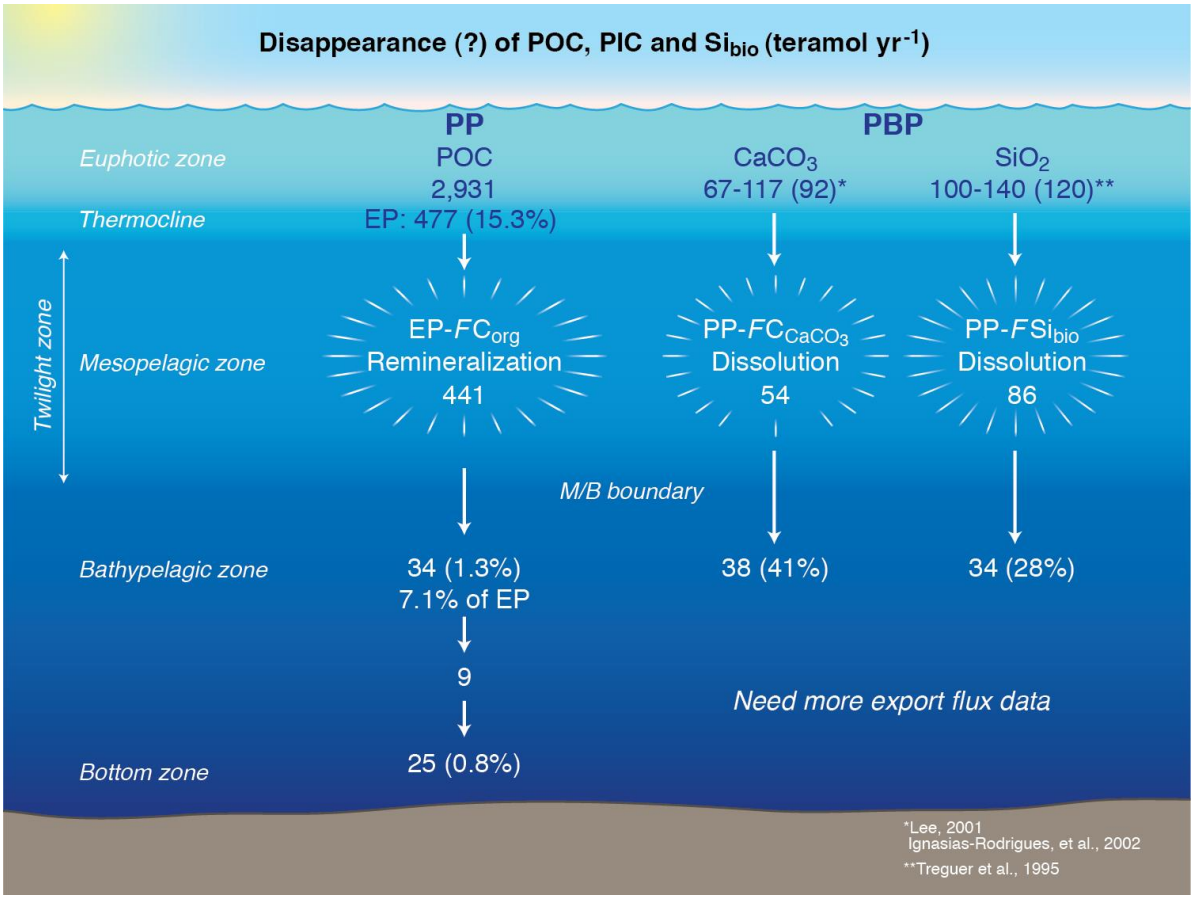
- POC vertically transported to the oceanic interior by aggregates and their ballasts, mainly $CaCO_3$ and biogenic opal, with a smaller role for lithogenic aerosols through the mesopelagic zone
- migrating zooplankton communities effect the vertical transport and remineralization of POC in the upper layers of the ocean
- the oceanic region exhibiting the highest POC flux over a significantly large region is the area of the North Pacific Boreal Gyres
- $F_{m/b}C_{org}$ and $F_{m/b}C_{inorg}$ are particularly high in large upwelling margins, including the divergent Arabian Sea and off Cape Verde
- the lowest flux over a significant region/basin is in the North Pacific subtropical/tropical gyres
- where C_{org}/C_{inorg} and Si_{bio}/C_{inorg} are < 1 defines the "Carbonate Ocean", and where these ratios are ≥ 1 defines the "Silica Ocean"
- the Carbonate Ocean occupies about 80 % of the present world pelagic ocean between the two major oceanographic fronts, the North Pacific Polar Front and the Antarctic Polar Front, and
- the Silica Ocean is found on the polar sides of these fronts
- the global ternary % ratios estimated from 152 TS-[sediment-]trap samples of the three elements are 35:32:33
- from our global $F_{m/b}C_{org}$ and a model estimate of the global export production, we estimate the regeneration rate of CO_2 through the mesopelagic zone by the biological pump is 441 teramolC yr^{-1} [therefore, the mesolepagic zone re-mineralizes > 90 % of the export production POC to $\sum CO_2$ (and DOC)]

Ternary plots

- global plot: all ternary ratios in the analytical data from all TS-trap samples (AO, PO, IO & SO)
- the solid red circle near the center of the graph is the nonweighted average of all ternary ratios from the individual sites
- different oceans with different ratios
- PO ratios f C_{org} & C_{inorg} more constant than in the AO → Figure B
- proportions of C_{org} & C_{inorg} change randomly with latitude of biogeochemical province (thick arrows)
- T% data points move toward T% maximum of Si_{bio} (and C_{inorg} minimum) as the mooring locations move poleward in both hemispheres
- Southern Ocean (not shown here) with a lot of silica driven export







- 3 petamolC = 10^{15} molC
- bathypelagic export ratio: 34:38:34, i.e. the same as in the ternary diagram

Global export to the ocean's interior

C_{org}	36.2 teramolC yr^{-1}	434 Tg yr^{-1}
C_{inorg}	33.8 teramolC yr^{-1}	406 Tg yr^{-1}
Si_{bio}	34.6 teramolC yr^{-1}	969 Tg yr^{-1}
Ca_{bio}	33.8 teramolC yr^{-1}	
Delivery at Ocean Floor (>2 km)		
C_{org}	24.8 teramolC yr^{-1}	297 Tg yr^{-1}
Global Biogeochemical Mole Ratio		
C_{org}/C_{inorg}	1.07	delivery: 0.7
Si_{bio}/C_{org}	1.05	delivery: 1.4
Si_{bio}/C_{inorg}	1.02	delivery: >1

Take – Home Messages:
- production of organic matter in the ocean acts as a vertical carbon pump, creating a carbon gradient between surface and deep ocean (the Biological Pump)
- primary production depends on light, but also on nutrients, including micronutrients, such as iron
- how much of the produced organic carbon is exported out of the euphotic zone depends on the food web
- exported fraction sinks and is being remineralized, vertical carbon flux decreases with depth
- most of POC is remineralized above 1000 m and NOT exported to the deep ocean

Week 7a – Terrestrial Carbon Cycling

7

- global distribution of terrestrial biomass → almost all of it in the tropics: Amazon basin, Central Africa & Southeast Asia
- climatic controls on net primary productivity (NPP) → high NPP rates also at higher latitudes in temperature climatic regions
- soil organic carbon stocks high in the tropics but even more so in boreal areas

Input and output of soil organic carbon (SOC)

input		output
net primary productivity	soil carbon stocks	CO_2 and CH_4
		DOC, POC and DIC
dependent on • climate • CO_2 • site fertility • hydrology • species composition		dependent on • temperature • water • oxygen • substrate quality • fire • physical & chemical protection • enzymes and inhibitors

Temperature and SOC
- "[...] increasing temperatures increased the rate of soil carbon output more than the input."
  - example: permafrost – represents > 50% of SOC globally and is comprised of fresh OM that is easy to degrade

Climate as a control on carbon turnover and storage in ecosystems
- high turnover times boreal areas due to not a lot of vegetation (it takes ~500 years) for carbon to overturn
- low turnover times in the tropics

Carbon turnover depending largely on
- *temperature*
- *water availability*
- *oxygen*
- *minerals*

Water and SOC
- regulates plant input into SOC & microbial community
- limit oxygen availability
- CH_4 production under anaerobic conditions

- example: peatland – 20-30% of the world's soil carbon stock & anaerobic conditions
- global peatland distribution largely in the higher latitudes, in boreal regions
- "the anaerobic conditions in peatlands prevent the enzyme phenol oxidase from eliminating phenolic compounds that inhibit biodegradation" → enzymes can enhance & prevent degradation of carbon in the soil

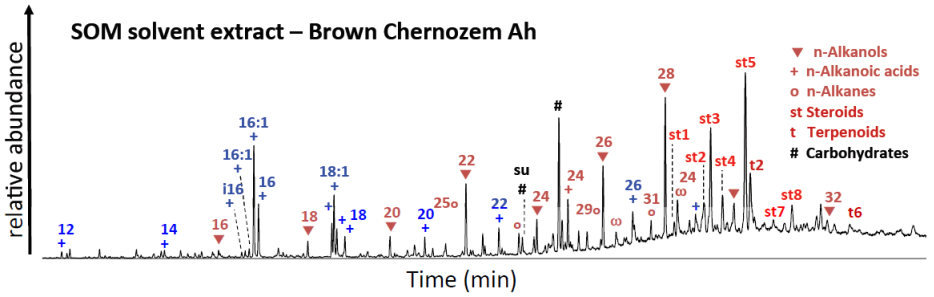
Mineral control on SOC content & turnover
- OM more difficult to be degraded when attached to minerals
- old carbon has slow turnover rates

Impact of fire on SOC storage
- fire regulates plant productivity and inputs into soils
- long-term (50a) annual burn in grasslands increased root C inputs and total SOC compared to controls
- produces charcoal or biochar, which is hard to break down and enhances carbon sequestration in soils (you can have very large build-up of charcoal which has a long turnover time)

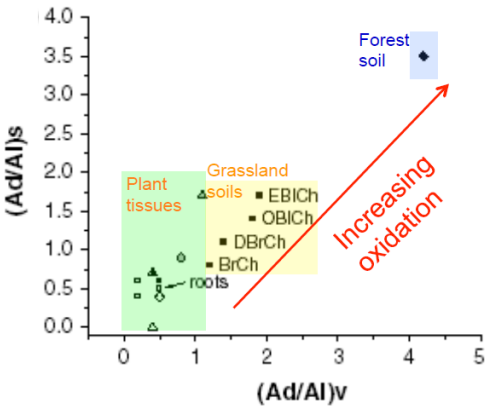
Concerns over soil organic matter under climate change
- potential for soils to destabilize (esp. permafrost) due to anthropogenic influence and rapidly degrade stored carbon
- key challenge is the heterogeneity of SOM → how do we disentangle OM fate and responses?
  - molecular information is needed

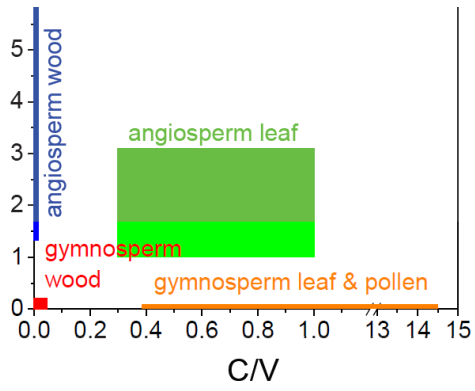
Plant inputs into SOM
1. waxy lipids → n-alkenes
2. cutin → major monomers
3. lignin
4. suberin → major monomers
5. cellulose
- 1/2/3 all related to long C-chains

Organic matter as a "fingerprint"
- longer time until signal peak ≙ larger boiling time inside the gas chromatographic instrument ≙ bigger molecules
- specific markers are used for specific plants
  - e.g. Diterpenoids for large plants like trees and driterpenoids for smaller plants like grasses and flowers



Lignin biomarkers
- angiosperm woods (normal tropical forest trees) with vanillyls only
- gymnosperm woods (big tropical forest trees) vanillyls and syringyls
- non-woody vascular plant tissues contain cinnamyls





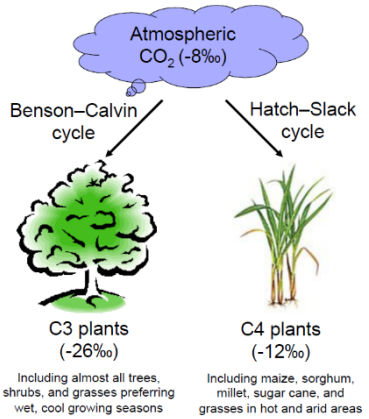
Information on lignin degradation

- acid/aldehyde ratio increases with increasing temperature
- ratio increases from plant tissues → grassland soils → forest soils

Lignin biomarkers
- *vanillyls phenols*
- *syringyls phenols*
- *cinnamyl phenols*

Information on Lignin source
- *gymnosperm woods: vanillyls only*
- *angiosperm woods: vanillyls & syringyls*
- *non-woody vascular plant tissues: contain cinnamyls*

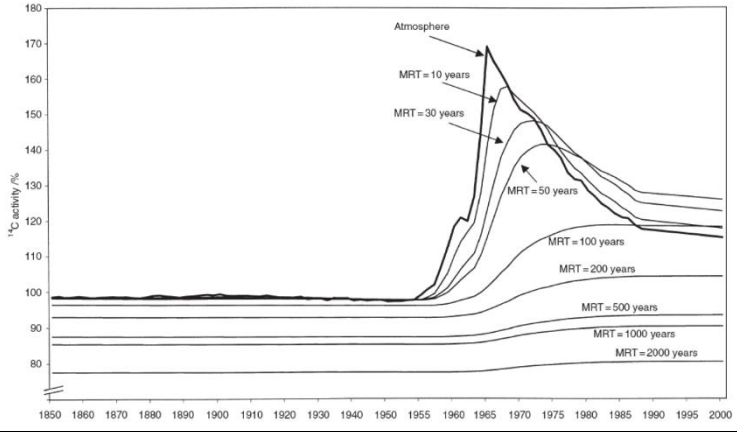
angiosperms *→ flowering plants, have seeds that are enclosed within an ovary (usually a fruit)*
gymnosperms *→ no flowers or fruits, and have unenclosed or "naked" seeds on the surface of scales or leaves (seeds often configured as cones)*



Response of SOM due to global warming
→ degradation vs. preservation
- cutin-derived compounds increase by a lot
- enhanced **lignin oxidation/degradation** after soil warming
- significant increase in acid biomarkers with higher T

^{13}C stable isotope analysis to study SOM cycling
- where the plant community changes between C_3 and C_4 plants, a simple two-compartment model can be used to estimate the proportion of C in the soil derived from the original and the new vegetation
- experiment done in 2010 by Feng et al. → In Free Air CO_2 Enrichment (FACE) Experiment
  - significant fraction of cutin and suberin is transformed into non-hydrolysable SOM (preservation) which may not be accounted for in the hydrolysable fraction of SOM

Studying soil C dynamics using ^{14}C
- estimate the "mean residence time" (MRT) of the steady-state soil organic matter on two different time scales
  - 10^2 to 10^3 years: natural radiocarbon
  - years to decades: bomb C – a conservative tracer → mean residence time of fast cycling SOM



Take – Home messages:
- minerals important for preserving carbon in soils
- mineral associated carbon turnover: flat

Week 7b – Terrestrial organic carbon inputs into the oceans

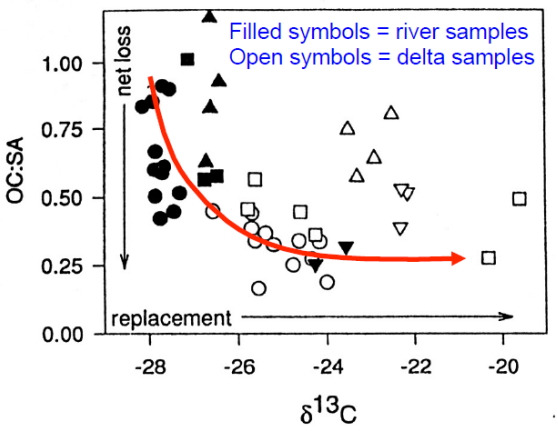
7b

- most (ca. 90%) of the OC burial in present-day marine sediments on continental margins and in deltas
- these depositional env. have potential to be strongly influenced by terrestrial organic carbon inputs
- the flux of POC from land is sufficient to account for all the OC being buried in marine sediments
- terrestrial OM is relatively poor in N relative to marine OM, and hence might be expected to be less susceptible to (re-)cycling (reduced respiration) and preferentially accumulate in marine OC reservoirs
  - this does not appear to be the case, so what happens to terrestrial OC?

Bulk properties used to quantify terrestrial OC inputs
- **C_{org}/ N ratios**
  - principle: vascular plant biomas is depleted in nitrogen (mainly composed of cellulose and lignin) compared to protein-rich marine phytoplankton
  - limitations: proteins are easily degradable, resulting in increased C_{org}/N ratios with degradation
- **$\delta^{13}C$ TOC composition**
  - principle: OC from marine primary production typically enriched in ^{13}C relative to C_3 vascular plant carbon
  - limitations: complications due to mixed inputs of C_3 and C_4 higher plant carbon
- organic C contents in sediments are generally tightly coupled to mineral surface area
  - the more surface area the mineral has the more %OC in the sediment
  - clay with more surface area than sand

- quantify your sample in regards to terrestrial & marine end members (sample may at a certain time have a composition of 70% terrestrial and 30% marine)

Loss of terrestrial OC and replacement by marine OC in deltaic systems
→ assumes mineral surface area is conserved during weathering and transport to the oceans



- as particles come from rivers: OC/SA ratio drops and $\delta^{13}C$ goes up
- loss of terrestrial carbon to marine carbon as mineral goes out into the open ocean
- less than 40% of terrestrial carbon remains on surface of minerals after leaving delta → efficient degradation

Biological markers as tracers of terrestrial OC inputs

- lignin-derived phenols can give information about
  - angiosperm vs. gymnosperm
  - leafy vs. woody vegetation
  - extent of lignin degradation
  - $\delta^{13}C$: determination of C_3 vs C_4 vs CAM inputs
  - ^{14}C: age of lignin or timescales of lignin transfer from litter to sediments
- sediments from Gulf of Mexico show angiosperm and leafy tissue signals → mostly grasses, weed, etc.

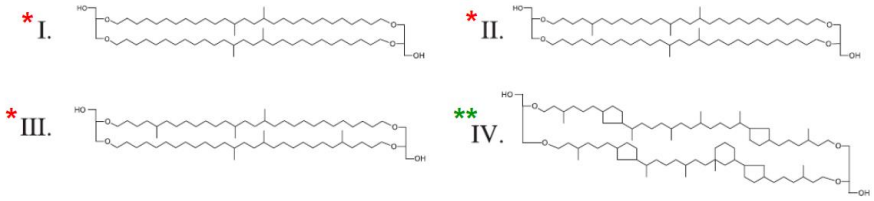
Molecular markers of terrestrial vegetation

- $\delta^{13}C$: determination of C_3 vs. C_4 vs CAM inputs
- δD: aridity/water stress
- ^{14}C: age or transfer time from litter to sediment
  → stable isotope ratios generally insensitive to degradation

Influence of long-term degradation on isotopic composition of leaf-vax biomarker lipids

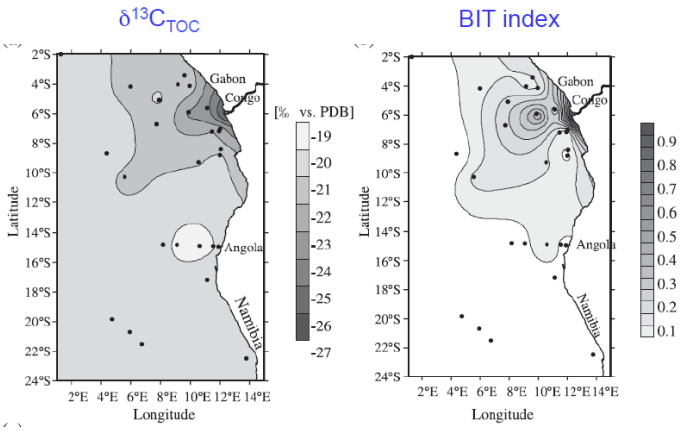
- while n-alkane percentage of modern content decreases rapidly with decomposition time (90% of biomarker degraded after 25 years), $\delta^{13}C$ values remain the same
  - good news everyone!

BIT index → a novel proxy for terrestrial organic matter in sediments based on branched and isoprenoid tetraether lipids



$$BIT = \frac{[I + II + III]}{[I + II + III + IV]}$$

- * ≙ derived from anaerobic soil bacteria
- ** ≙ derived from non-thermophilic archaea
- index shows the amount of soil carbon that comes into the sediment instead of plant-based carbon
- example case: African west coast
  - in deltaic region: high $\delta^{13}C$ values, i.e. terrestrial sediments
  - BIT index shows high values, i.e. soil derived carbon instead of plant-derived carbon → most of sediments from soil carbon



Evidence for minimal terrestrial OC contributions to marine sediments

- low C_{org}/N values for marine sediments

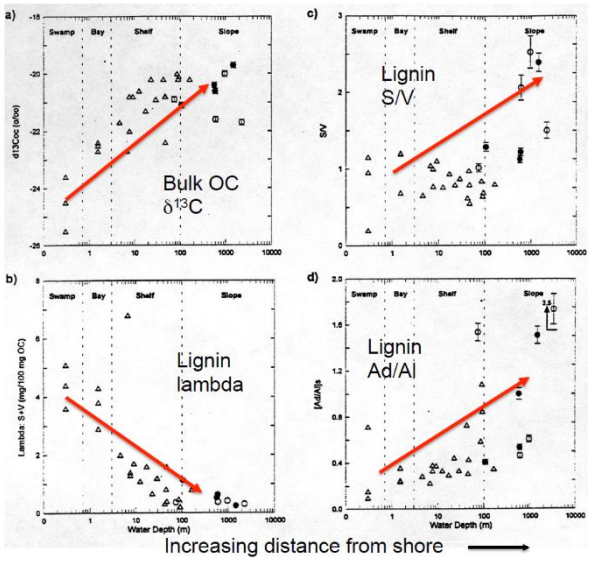
- enriched $\delta^{13}C$ values of marine sedimentary OC relative to terrestrial (C_3 OC)
- rapid decrease in lignin phenols and other molecular proxies of terrestrial organic matter with increasing distance offshore / from river mouth

Evidence for <u>significant</u> terrestrial OC contributions to marine sediments

- contributions from ^{13}C-enriched (C_4) terrestrial OC sources?
- importance of hydrodynamic processes in export of terrestrial organic compounds
- widespread distribution of plant wax lipids in ocean sediments
- greater importance of terrestrial OC in glacial times (low sea-level stand, direct river discharge to continental slope)?
- most logical source of old carbon: from old soils

Compositional & isotopic analyses of Gulf of Mexico sediments

- with increasing distance from the shore, $\delta^{13}C$ increases
  - $\delta^{13}C$ increases in warm ocean conditions



Take – Home Messages:

- annual export of terrestrial OC by rivers to the oceans is more than sufficient to account for all the OC buried in marine sediments
- the majority of OC burial in marine sediments takes place on the continental margins, particularly in deltaic systems
- together, these two observations imply that terrestrial organic matter may comprise a major fraction of OC buried in marine sediments
- nevertheless, a range of evidence indicates that terrestrial OC is efficiently remineralized before or upon entering the ocean
- current estimates for terrestrial OC burial may be incorrect/too low due to:
  - inadequate sampling of small [tropical] mountainous river systems
  - inadequate characterization of rivers draining into the Arctic Ocean
  - variable inputs of C_3 and C_4 terrestrial vegetation
  - compositional transformations attending dispersal of terrestrial OM in the oceans