Quimioestratigrafia isotópica: conceituação

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O que é a Quimioestratigrafia?

- Estratigrafia química, ou Quimioestratigrafia, é o estudo das variações da composição química de sedimentos e rochas sedimentares ao longo de uma sucessão estratigráfica.

- Funciona de maneira semelhante à litoestratigrafia ou à bioestratigrafia

Quimioestratigrafia isotópica

- Ramo especializado da Quimioestratigrafia.

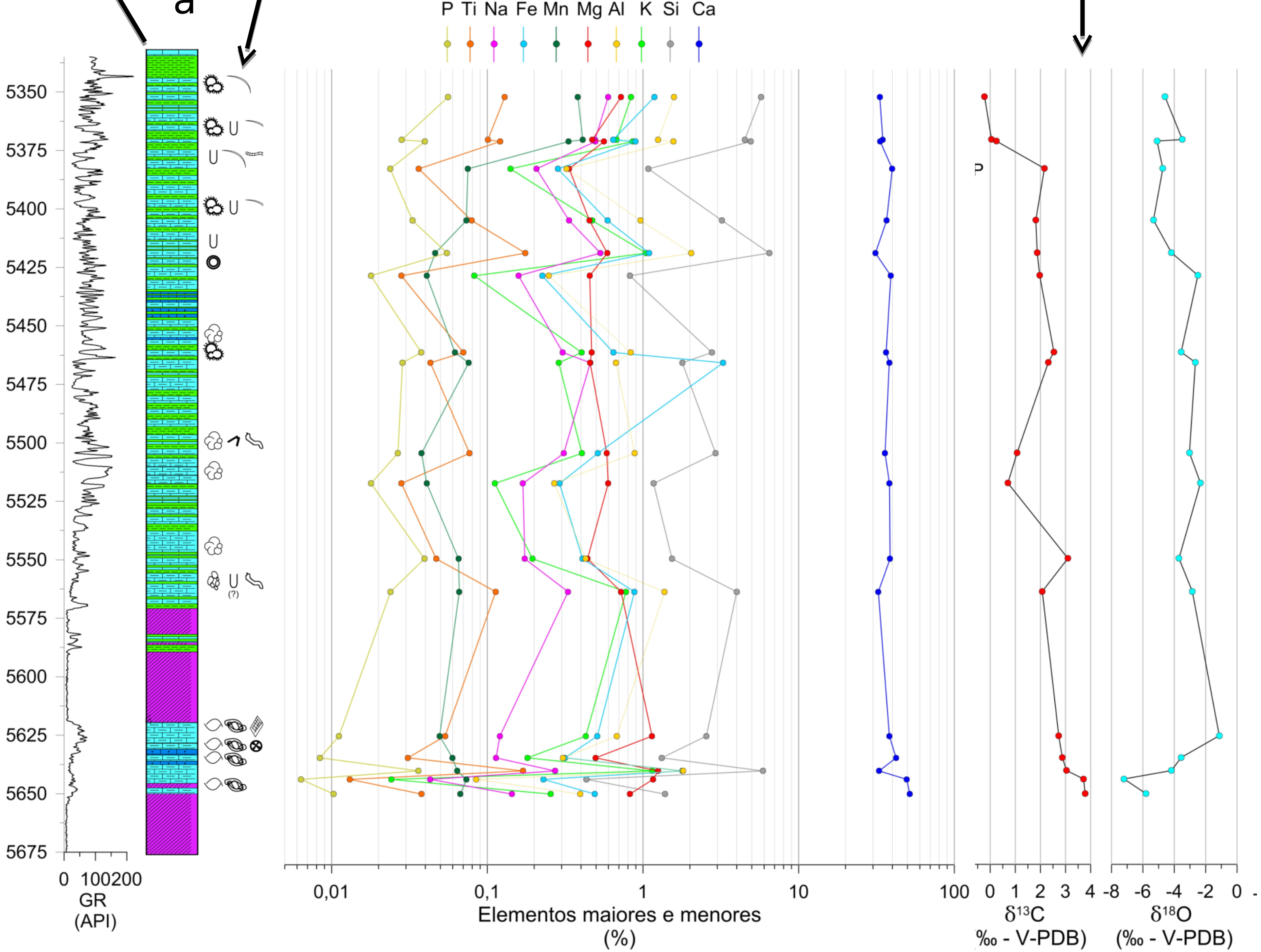
- Estudo das variações da composição ***isotópica*** de sedimentos e rochas sedimentares ao longo de uma sucessão estratigráfica.

Litoestratigrafia

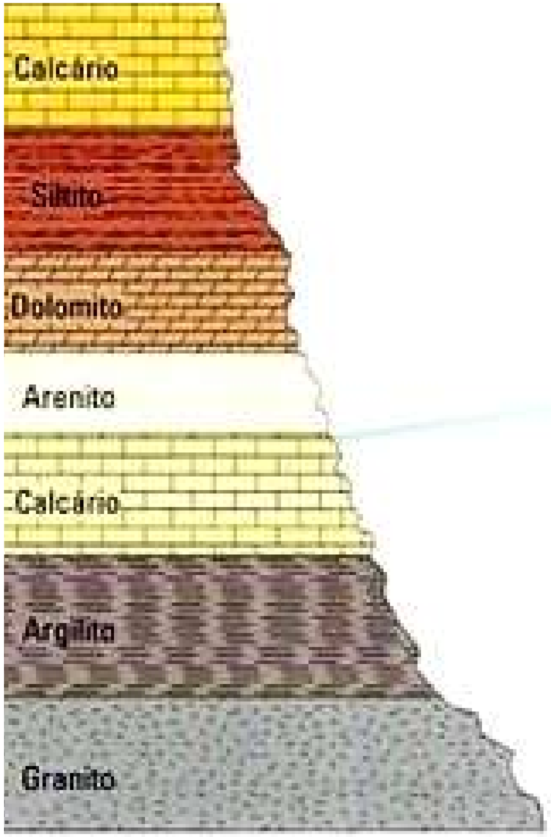
Bioestratigrafia

Quimioestratigrafia

Quimioestratigrafia Isotópica



Que tipo de informação a quimioestratigrafia isotópica fornece?



Rochas siliciclásticas:

Composição geoquímica reflete dominantemente a composição da fonte (ou mistura de fontes)

Quase um estudo de proveniência...

Rochas sedimentares de origem **bioquímica**:

Precipitados autigênicos de uma bacia

Podem guardar a composição química e isotópica da coluna d'água no momento

Reconstruções Paleoambientais !!!

O que cada elemento ou sistema isotópico nos diz?

- Cada sistema isotópico analisado nos sedimentos tem um significado geológico.

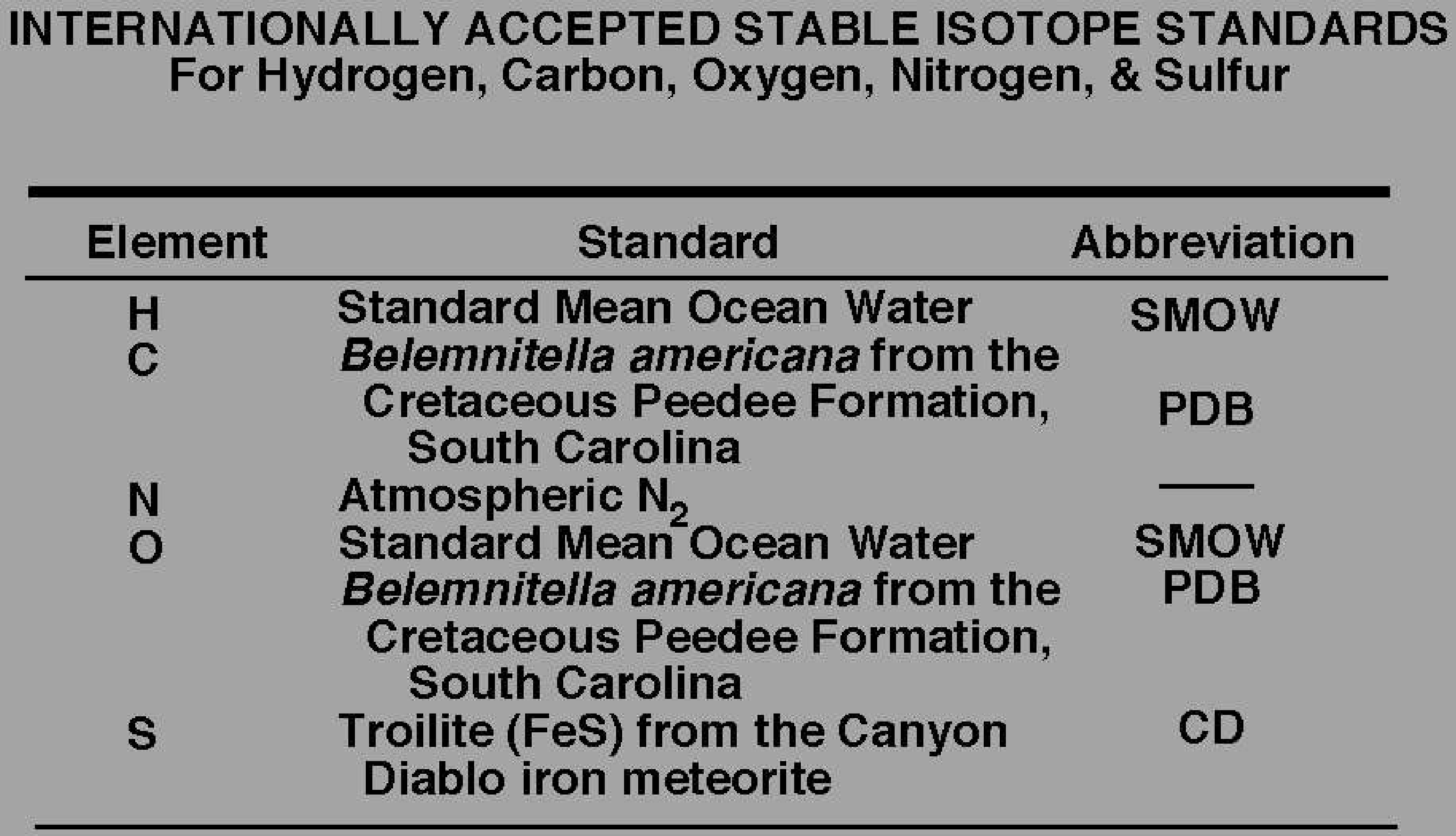
- *Proxies* (traçadores): bioprodutividade, estado redox, pH, tectônica...

- Cada elemento possui:
  - Ciclo geoquímico próprio no planeta
  - Fracionamento isotópico particular

OXYGEN ISOTOPES

B.C. Schreiber
U. Washington
Dept. Earth & Space Science

Standards Vary



INTERNATIONALLY ACCEPTED STABLE ISOTOPE STANDARDS
For Hydrogen, Carbon, Oxygen, Nitrogen, & Sulfur

Element	Standard	Abbreviation
H	Standard Mean Ocean Water	SMOW
C	*Belemnitella americana* from the Cretaceous Peedee Formation, South Carolina	PDB
N	Atmospheric N_2	—
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S	Troilite (FeS) from the Canyon Diablo iron meteorite	CD

From: *Stable Isotope Geochemistry*, J. Hoefs, 1980

Oxygen isotope chemostratigraphy

Relative concentrations (stable isotopes):

^{16}O = 99.76%

^{17}O = 0.38%

^{18}O = 0.21%

Urey and Emiliani (1947) discovered that oxygen isotopes fractionate, depending largely on temperature. They examined shells of foraminiferans throughout the Pleistocene and O isotopes in the shells appeared to respond to the **temperature** changes associated with the ice ages, with **oceanic sediments becoming isotopically heavy during glaciations and lighter during warming**.

BUT

Normally, when when water evaporates, molecules with ^{16}O more readily enter the vapor phase. Typically this makes no difference as the water soon condenses and is back in the oceans.

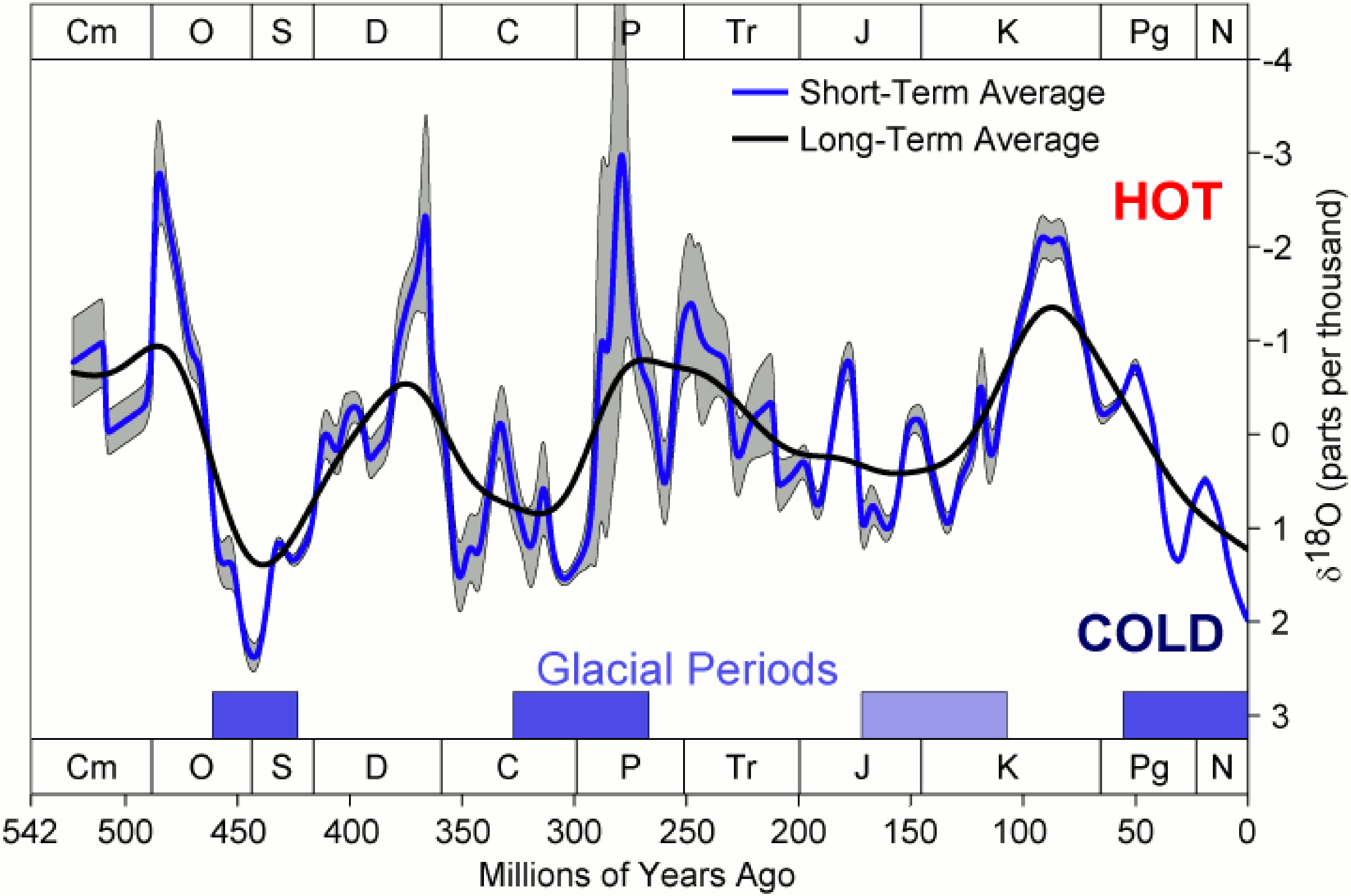
The same principle applies to atmospheric water. Condensation preferentially draws $H_2{}^{18}O$ out of the atmosphere. Results in ^{16}O-rich (or ^{18}O-depleted) polar snow.

During times of high glacial activity, ocean waters are very enriched in ^{18}O

Organisms that incorporate oxygen-bearing molecules (such as $CaCO_3$) into shells or bones will also be enriched in ^{18}O. Therefore, a $\delta^{18}O$ curve is a direct result of ice volume.

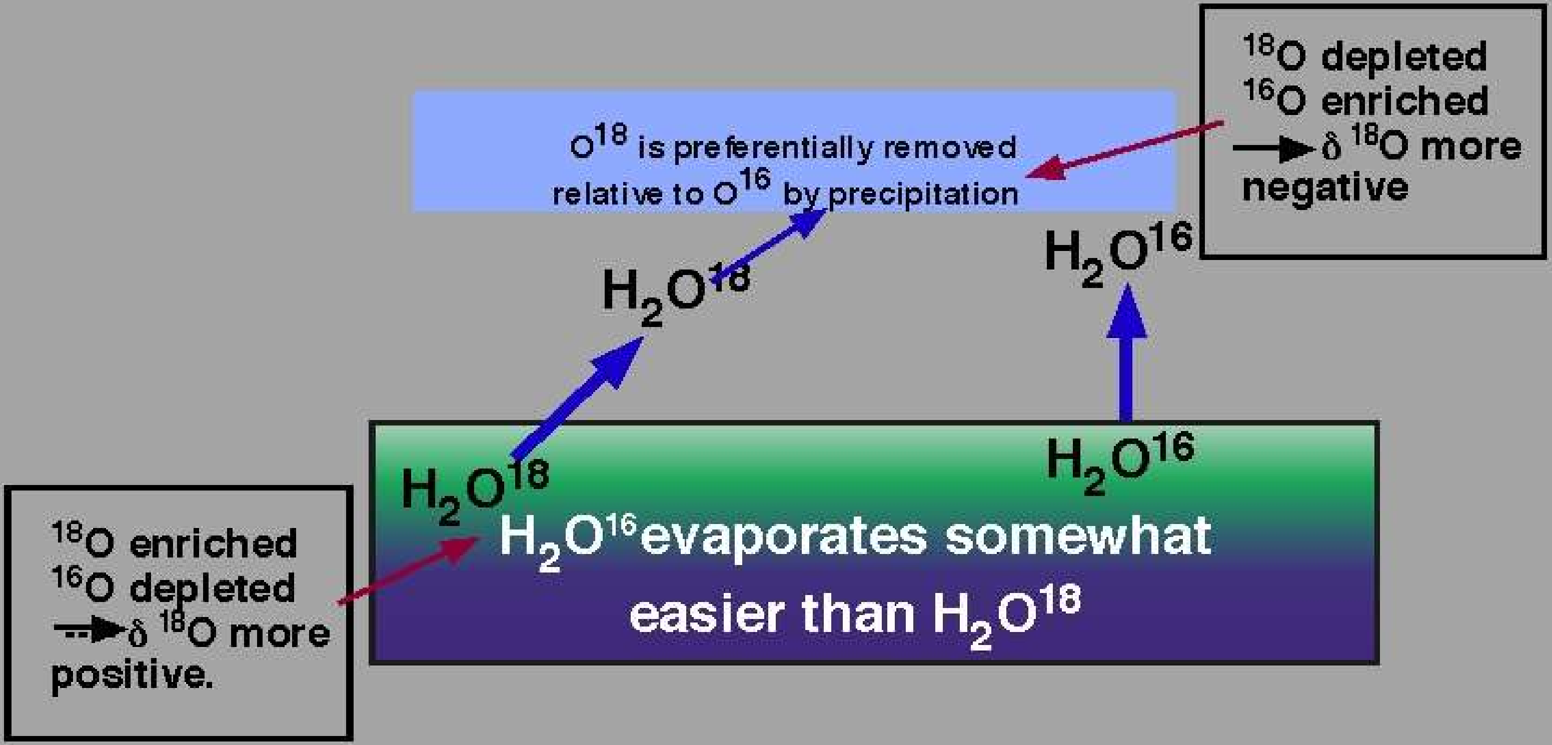
So the $\delta^{18}O$ curve is a fairly good proxy for temperature changes

Phanerozoic Climate Change



ISOTOPE FRACTIONATION

Enrichment process (isotope fractionation): the lighter ^{16}O evaporates first. The heavier ^{18}O condenses out first.



^{18}O depleted
^{16}O enriched
→ $\delta\,^{18}O$ more negative

O^{18} is preferentially removed relative to O^{16} by precipitation

H_2O^{18}

H_2O^{16}

H_2O^{18}

H_2O^{16}

H_2O^{16} evaporates somewhat easier than H_2O^{18}

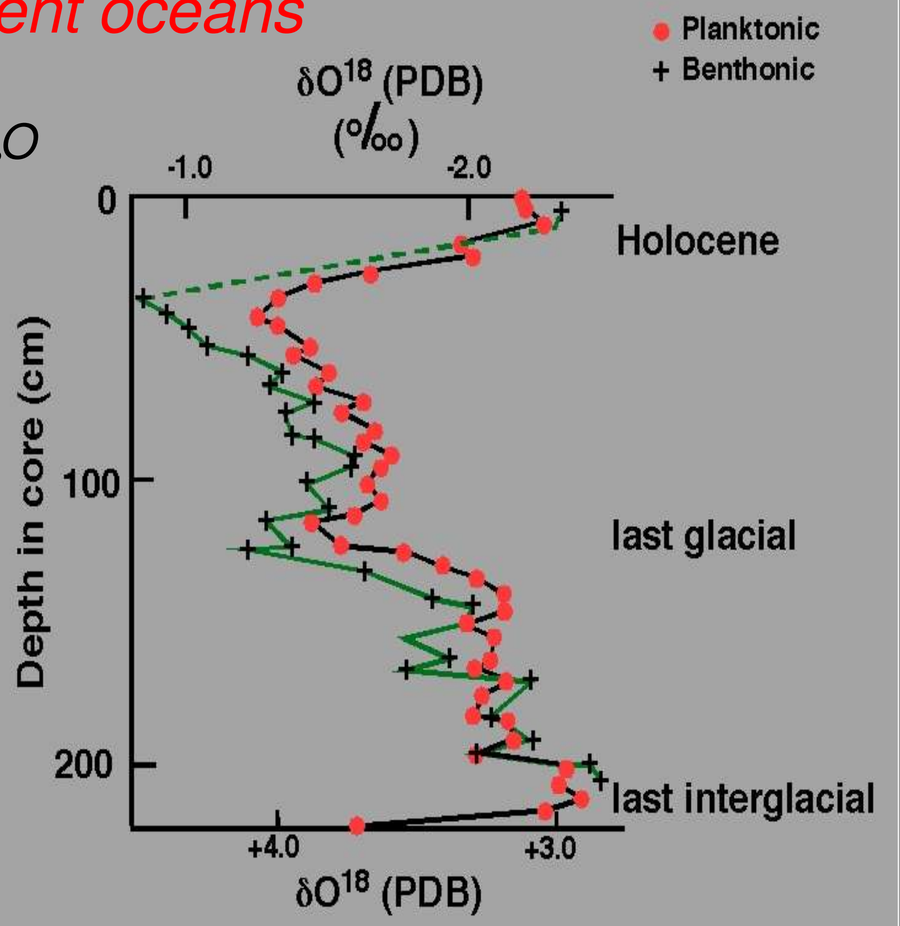
^{18}O enriched
^{16}O depleted
→ $\delta\,^{18}O$ more positive.

Estimation of temperature in ancient oceans

$CaCO_3(s) + H_2{}^{18}O \Leftrightarrow CaC^{18}OO_2 + H_2O$

The exchange of ^{18}O between $CaCO_3$ and H_2O

The distribution is Temperature dependent



$\delta^{18}O$ of planktonic & benthic foraminifera:
piston core V28-238 (160ºE 1ºN)

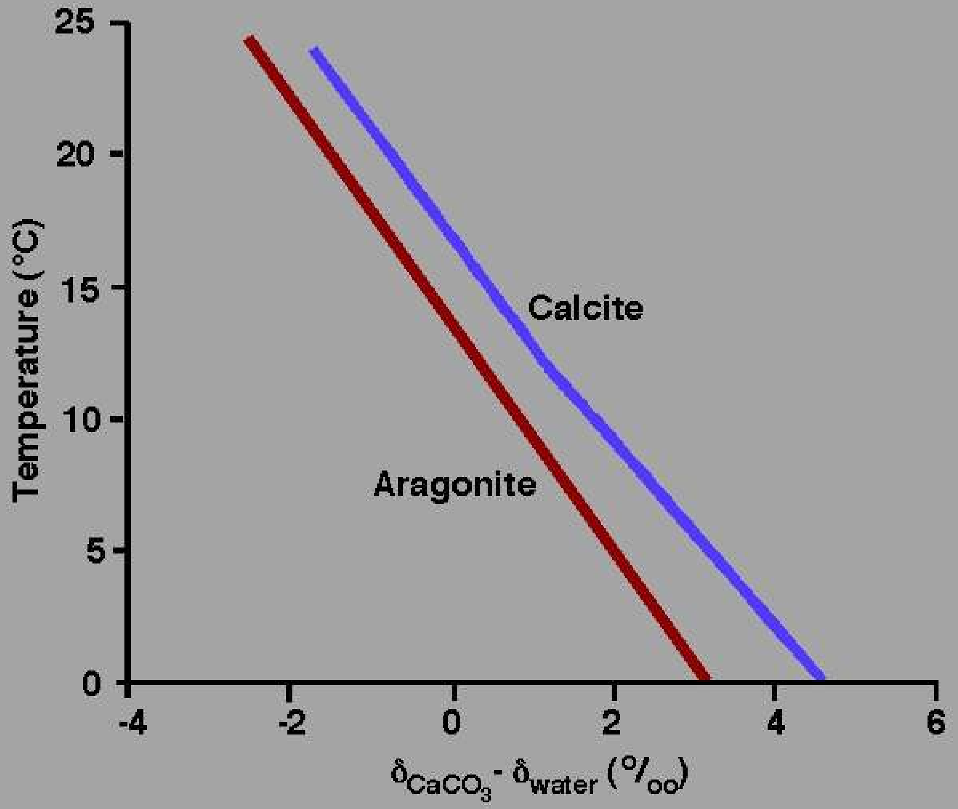
Planktonic and Benthic foraminifera differ due to differences in water temperature where they grow.

Planktonic forams measure sea surface T
Benthic forams measure bottom T

Assumptions:

1. ***Organism ppted $CaCO_3$ in isotopic equilibrium with dissolved CO_3^{2-}***
2. ***The $\delta^{18}O$ of the original water is known***
3. ***The $\delta^{18}O$ of the shell has remained unchanged***

δ^{18}O in $CaCO_3$ varies with Temperature

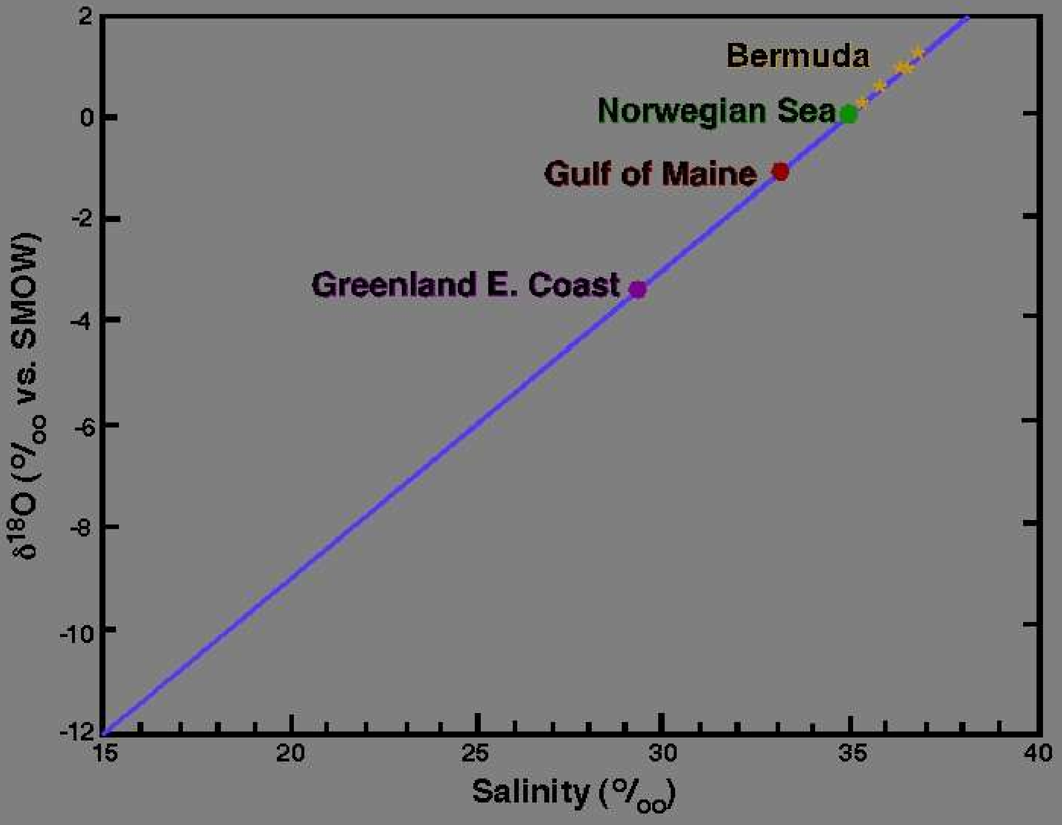


from lab experiments

Ehleringer & Hall, 1993 Fig 5.3

Complication: Changes in ice volume also influence δ^{18}O
More ice = higher salinity = more δ^{18}O left in the ocean

δ^{18}O increases with salinity



Simplified from data in Dansgaard, 1964 & Rozanski, 1993

Raleigh Fractionation -

Combination of both equilibrium and kinetic isotope effects

Kinetic when water molecules evaporate from sea surface

Equilibrium effect when water molecules condense from vapor to liquid form

Any isotope reaction carried out so that products are isolated immediately from the reactants will show a characteristic trend in isotopic composition.

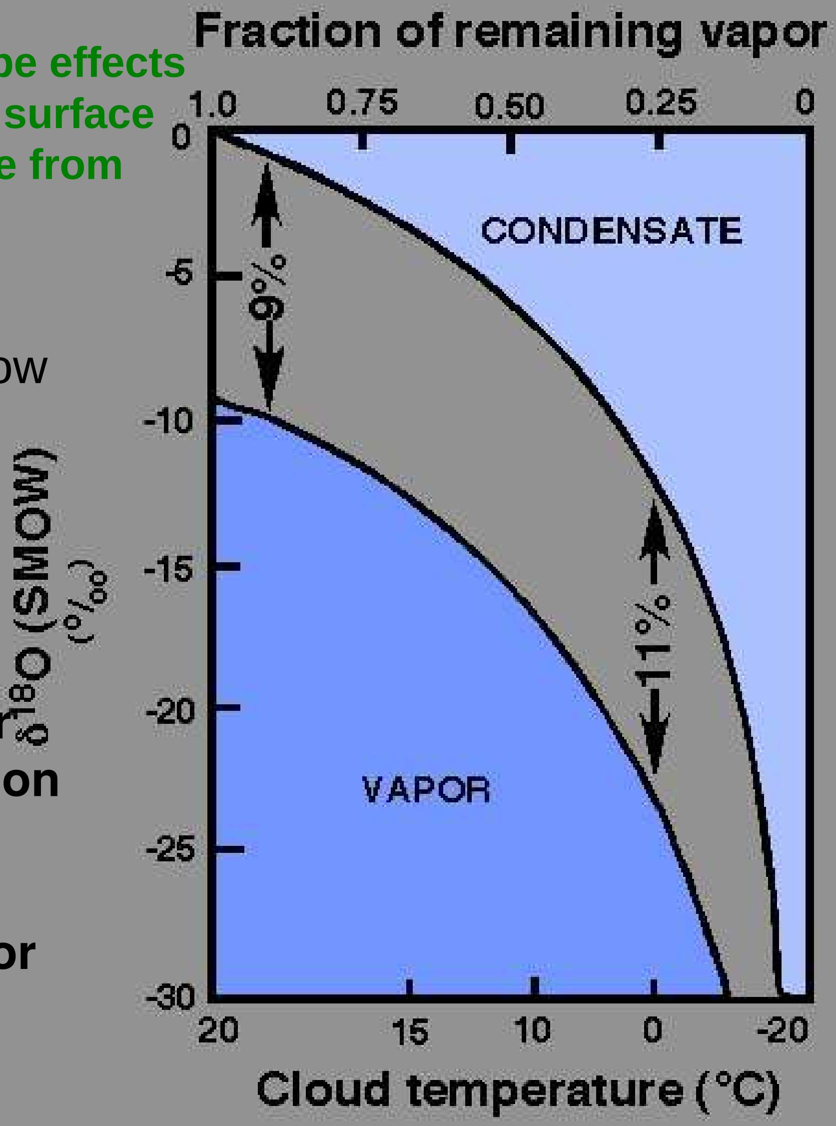
Example: Evaporation – Condensation/ Processes

$\delta^{18}O$ in cloud vapor and condensate (rain) plotted versus the fraction of remaining vapor for a Raleigh process. The isotopic composition of the residual vapor is a function of the fractionation factor between vapor and water droplets. The drops are rich in ^{18}O so the vapor is progressively depleted in ^{18}O .

Where $R_{vapor} / R_{liquid} = f^{(\alpha-1)}$

where f = fraction of residual vapor

$\alpha = R_l/R_v$



Fractionation increases with decreasing temperature

Distillation of meteoric water – large kinetic fractionation between ocean and vapor. Rain, forming in clouds, is in equilibrium with vapor and is heavier that the vapor. Vapor becomes progressively lighter. δD and $\delta^{18}O$ get lower with distance from source.

Water evaporation has a kinetic effect.

Vapor is lighter than liquid. At 20ºC the difference is 9‰ (see Raleigh plot).

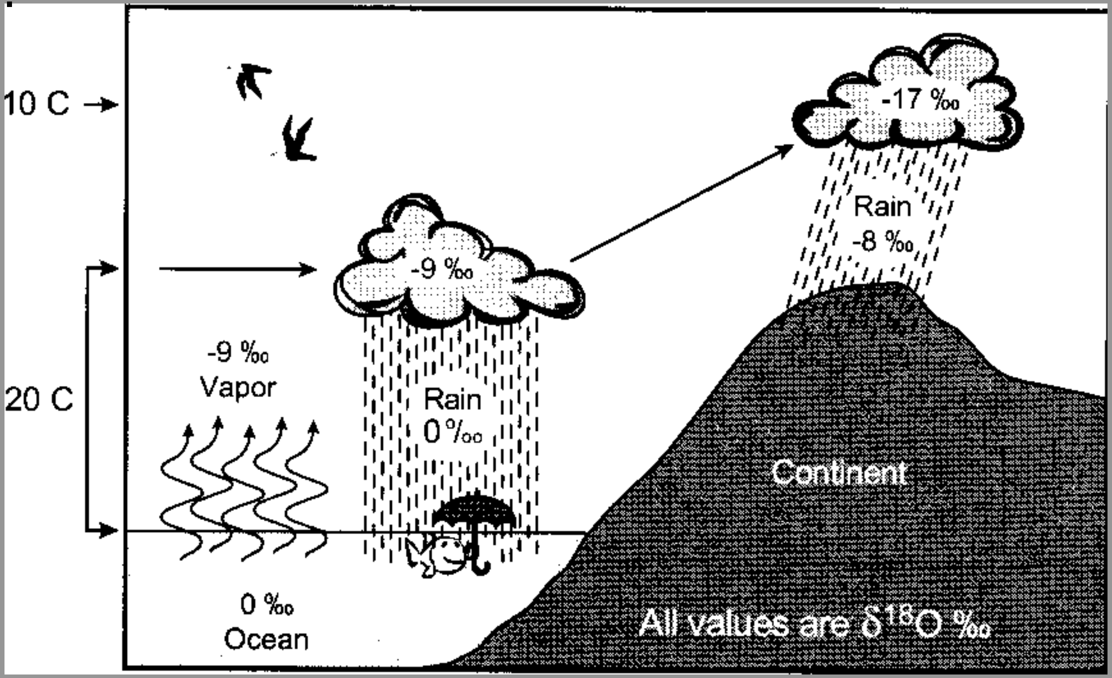
Also the energy required for vaporization of $H_2^{18}O$ is greater than for $H_2^{16}O$

Air masses transported to higher latitudes where it is cooler.

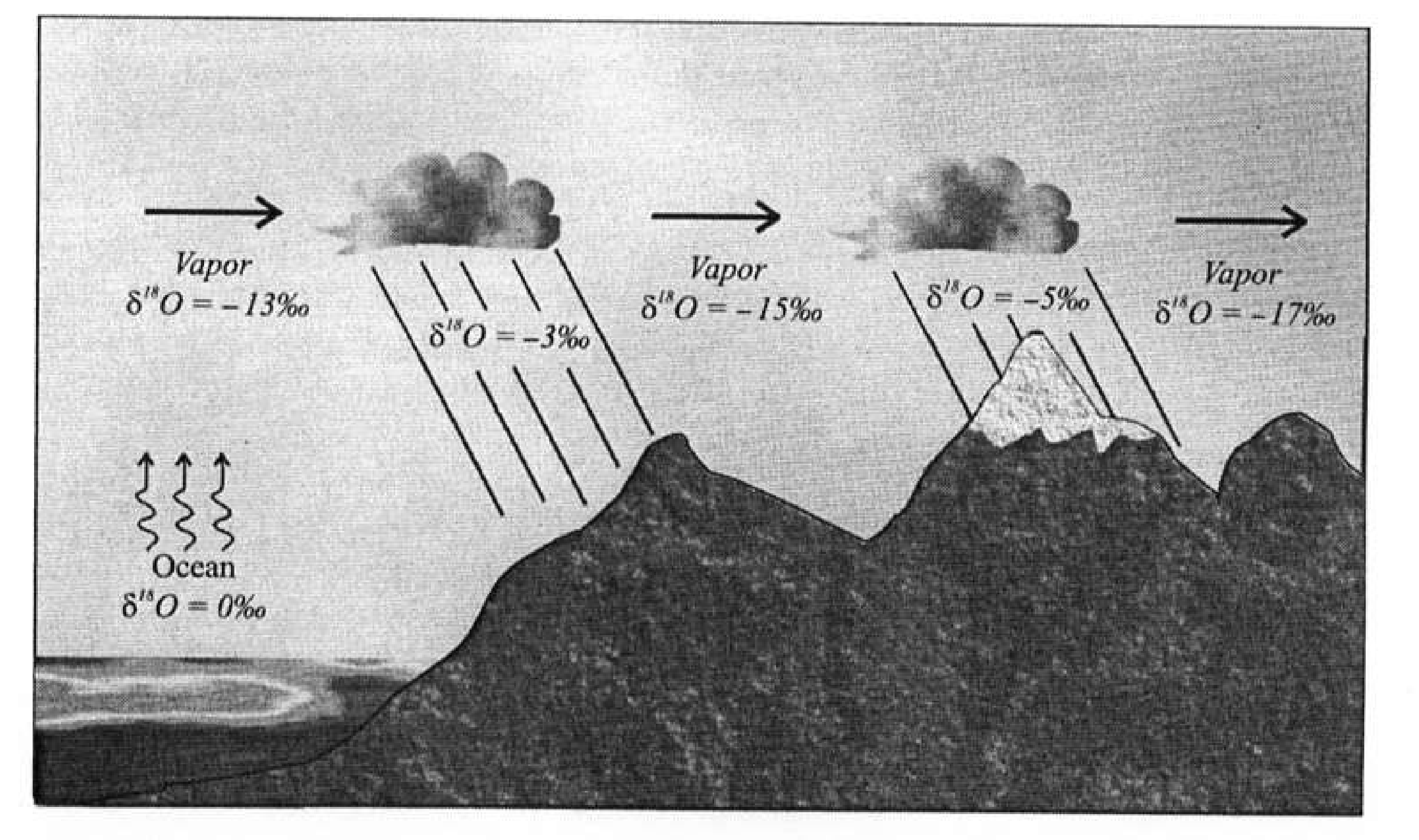
water lost due to rain

raindrops are rich in ^{18}O relative to cloud.

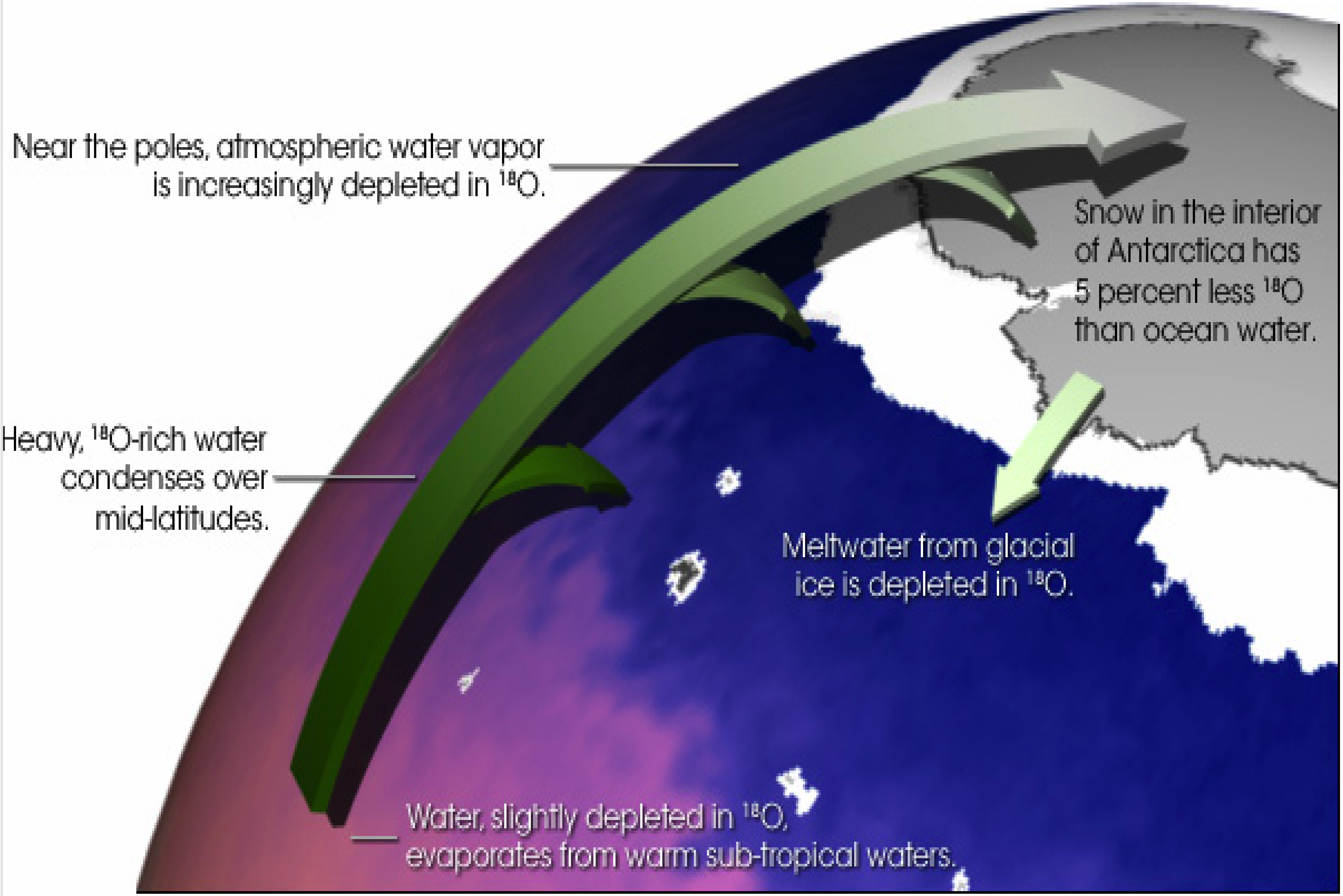
Cloud gets lighter



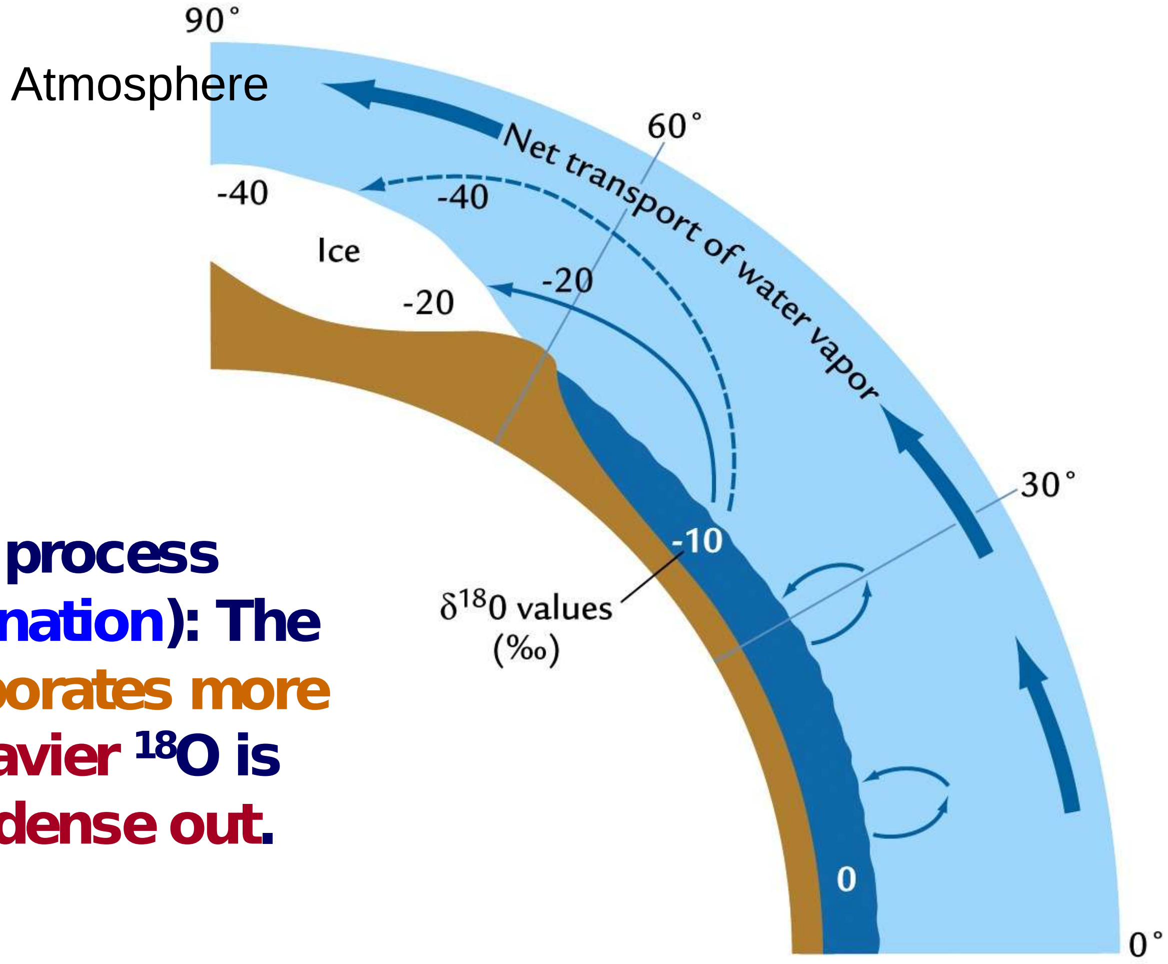
OCEANIC WATER VAPOR MODIFIED OVER LAND



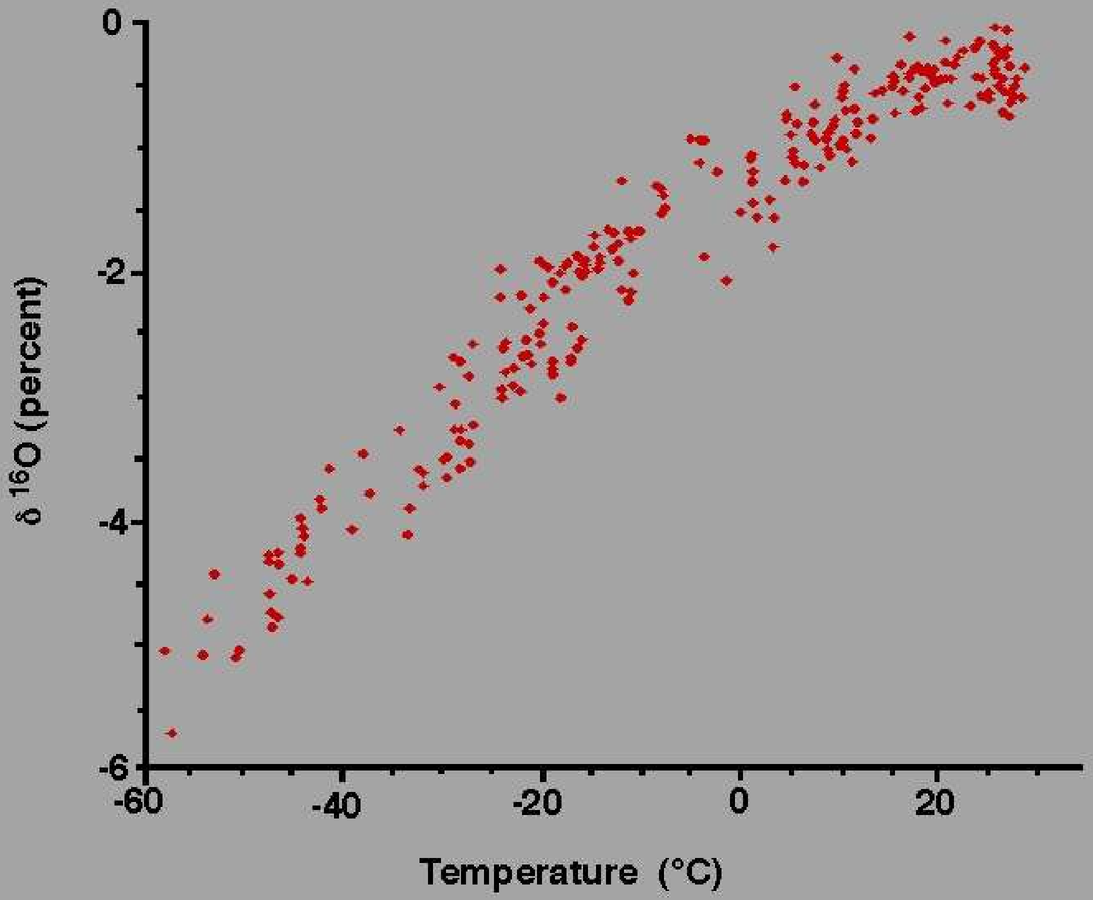
NASA, Earth Observatory, figure on-line



Isotope Fractionation



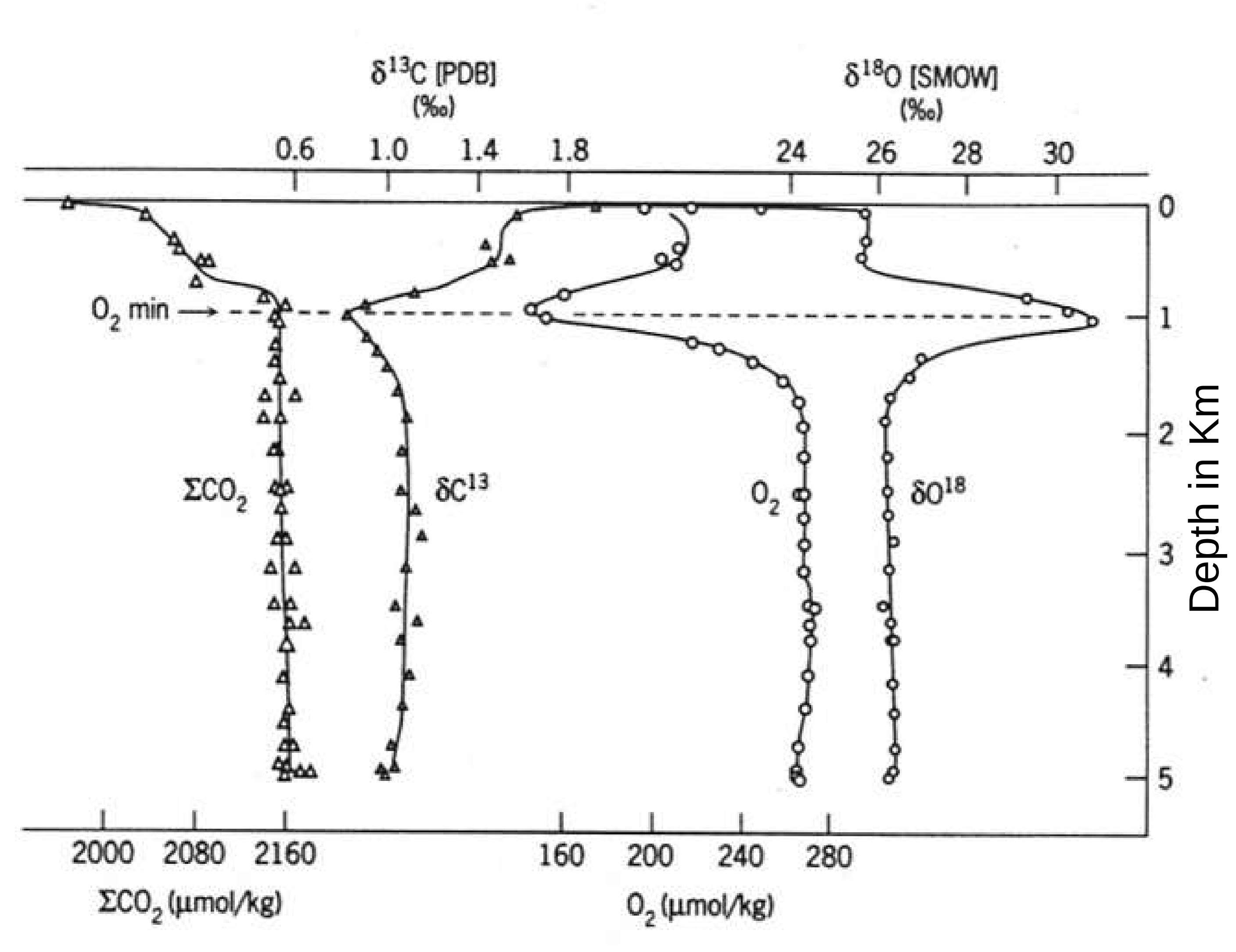
Enrichment process (isotope fractionation): The lighter ^{16}O evaporates more easily. The heavier ^{18}O is easier to condense out.



The concentration of ^{18}O in precipitation decreases with temperature. This graph shows the difference in ^{18}O concentration in annual precipitation compared to the average annual temperature at each site. The coldest sites, in locations such as Antarctica and Greenland, have about 5 percent less ^{18}O than ocean water.

(Graph adapted from Jouzel *et. al.,* 1994)

Vertical profiles of ΣCO_2, $\delta^{13}C$ in DIC, O_2 and $\delta^{18}O$ in O_2

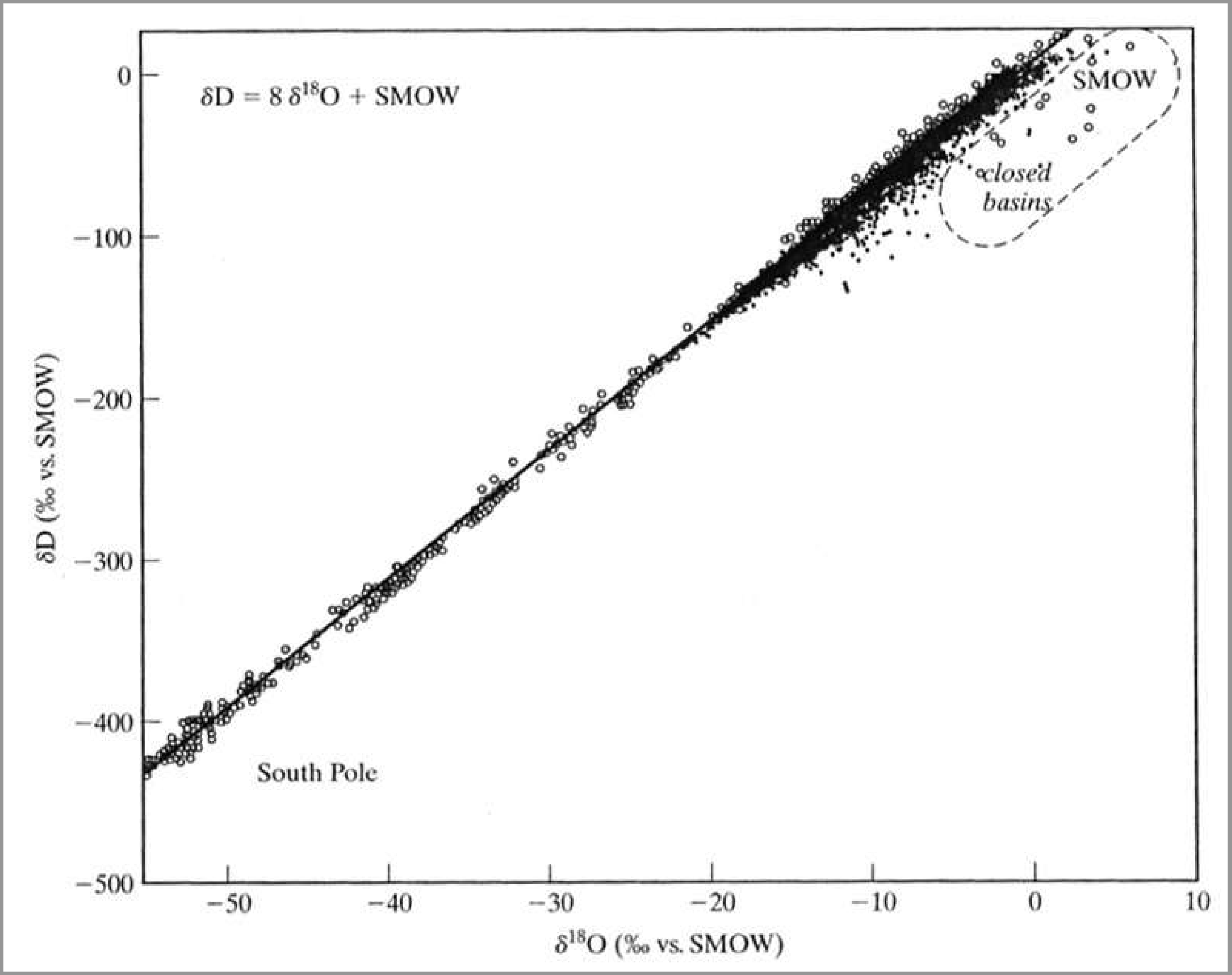


Depth in Km

North Atlantic data

Meteoric Water Line

Linear correlation between δD and $\delta^{18}O$ in waters of meteoric origin

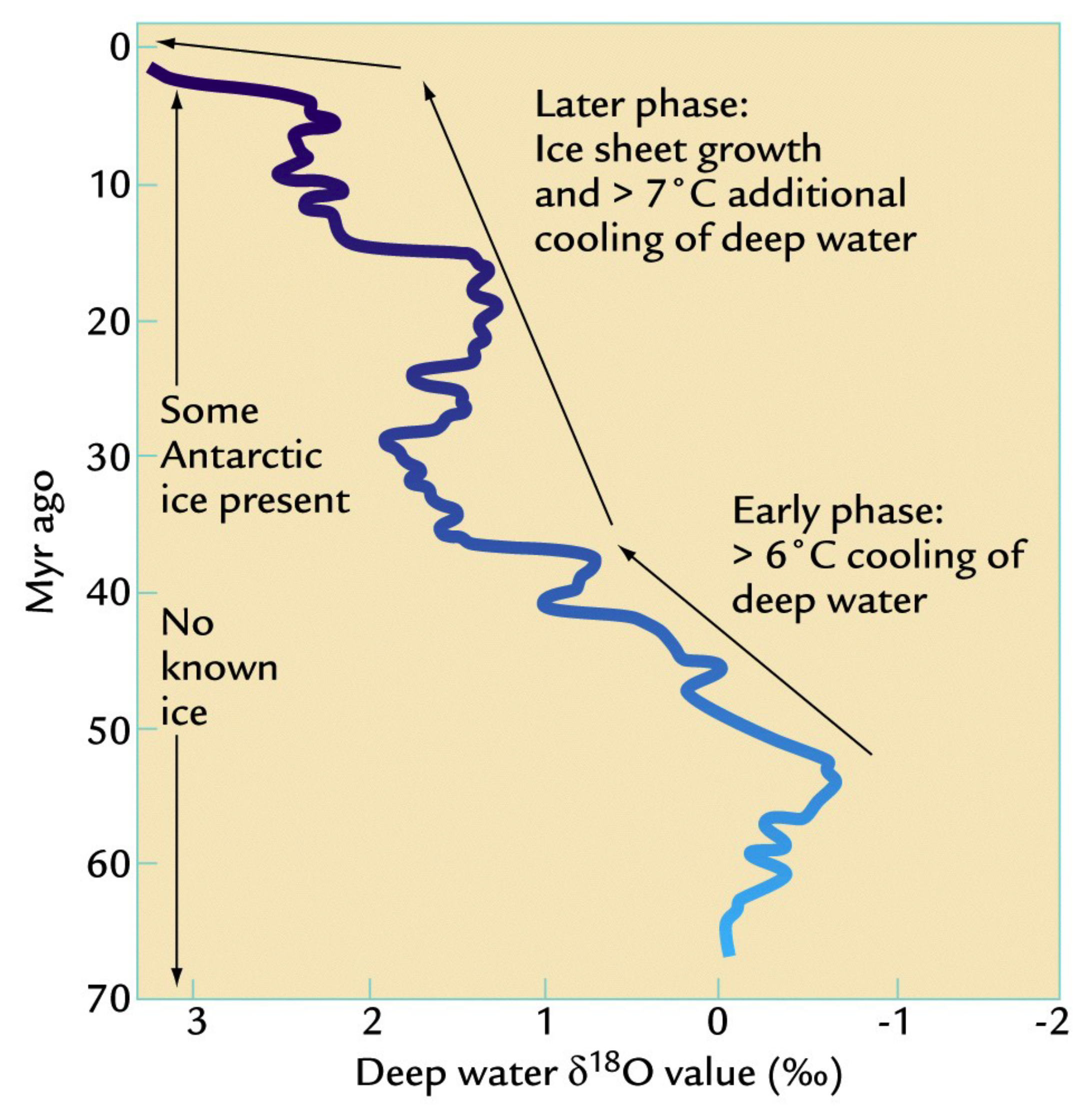


Long-term $\delta^{18}O$ trend in the deep ocean as measured from the calcite shells of foraminifera

Two factors:

(1) Changes in deep-ocean temperatures

(2) Growth of ice sheets on land (^{16}O enriched)



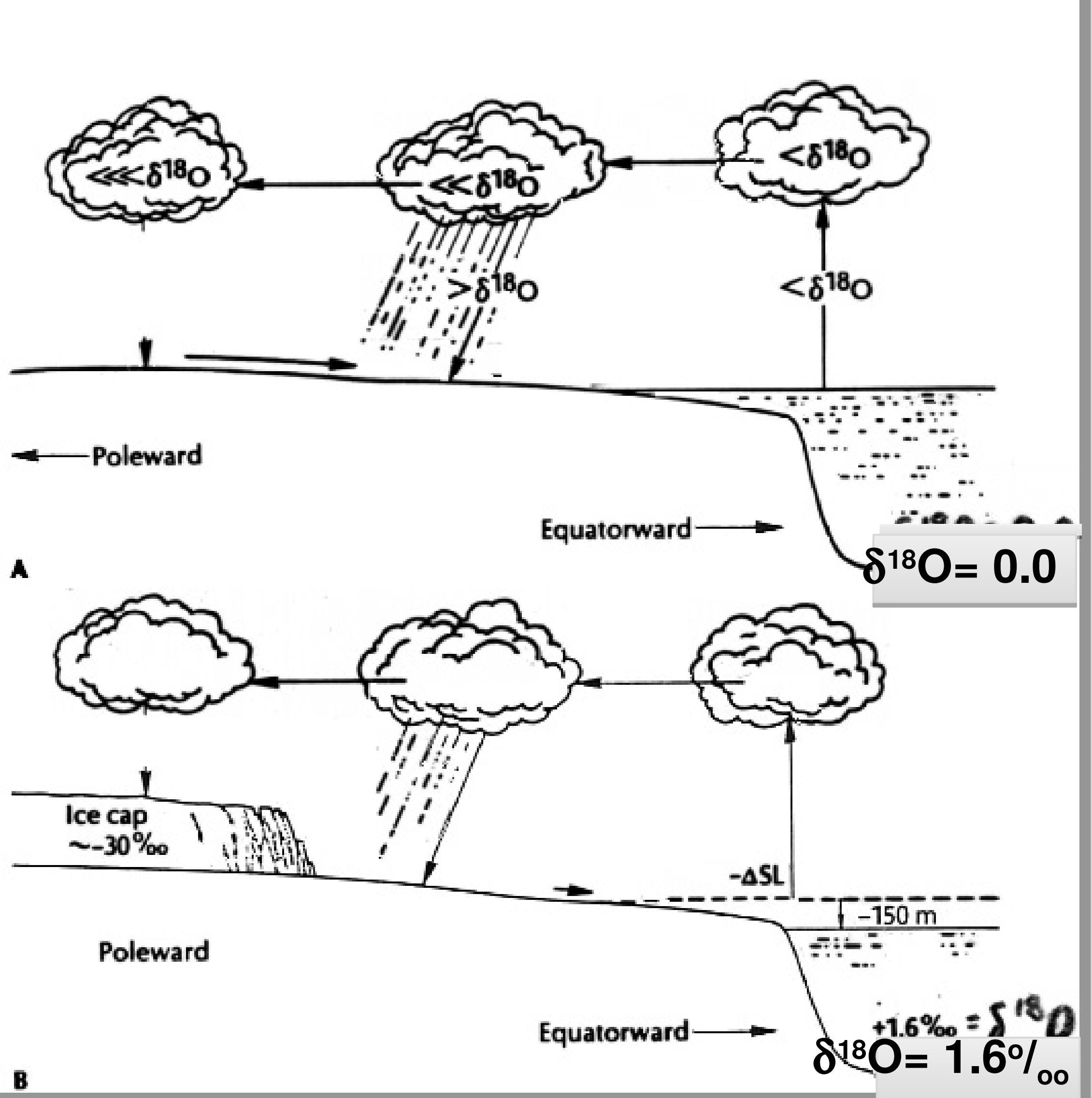
Oxygen isotope ratios as a thermometer

Precipitation has less ^{18}O than ocean, why?

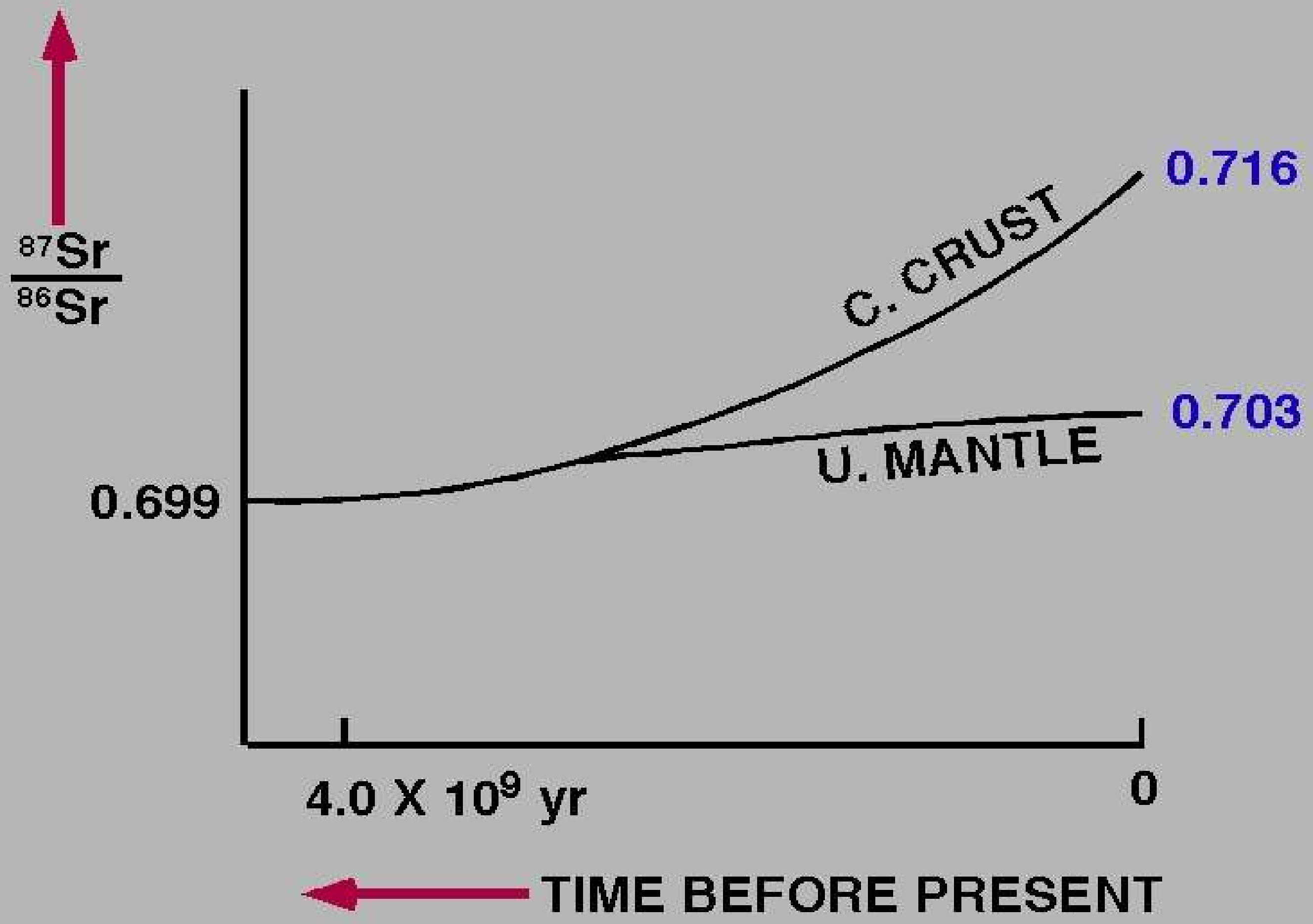
^{18}O content of precipitation at the given latitude decreases with decreasing temperature.
Why?

The less ^{18}O found in the glacier ice, the colder the climate.

OXYGEN ISOTOPES AND CLIMATE CHANGE



EVOLUTION OF ^{87}Sr/^{86}Sr RATIOS FROM BULK EARTH RATIOS SINCE FRACTIONATION



Elderfield, 1986

CARBON ISOTOPES

Standards Vary

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For Hydrogen, Carbon, Oxygen, Nitrogen, & Sulfur

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S	Troilite (FeS) from the Canyon Diablo iron meteorite	CD

From: *Stable Isotope Geochemistry*, J. Hoefs, 1980

3 basic, fairly stable isotopes of Carbon, C^{12}, C^{13}, and C^{14} C^{14} is present only in trace amounts & breaks down to N^{14} over time, leaving only 2 stable isotopes

^{12}C	98.89‰
^{13}C	1.11‰

2 basic isotopes of stable Carbon, C^{12} and C^{13} isotopes

Carbon exists in oxidized, elemental and reduced forms.

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As in the case of almost all compounds, the heavy isotope, C^{13} becomes concentrated in the more oxidized forms.

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The metabolic reduction of carbon (into organics) strongly partitions the C^{12} and concentrates the C^{12} in the organics.

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The metabolic reduction of carbon (into organics) strongly partitions the C^{12}, leaving the C^{13} in the more oxidized forms and concentrates the C^{12} in the organics.

Assuming that most of the original C on Earth began as volcanic CO_2 emissions, massive biologically induced reduction of carbon led to the concomitant production of the free oxygen (O_2) present in the atmosphere today.

THE PRESENT (LATE ARCHEAN ONWARD) AND MOST COMMON BIOLOGICAL CARBON CYCLE INVOLVES THE UTILIZATION OF CO_2 TO MAKE ORGANIC MATTER

2

IT REQUIRES THE PRESENCE OF AN OXIDANT, O_2 OR SO_4

IT IS IS DRIVEN EITHER CHEMICALLY OR BY “SOLAR-POWER”

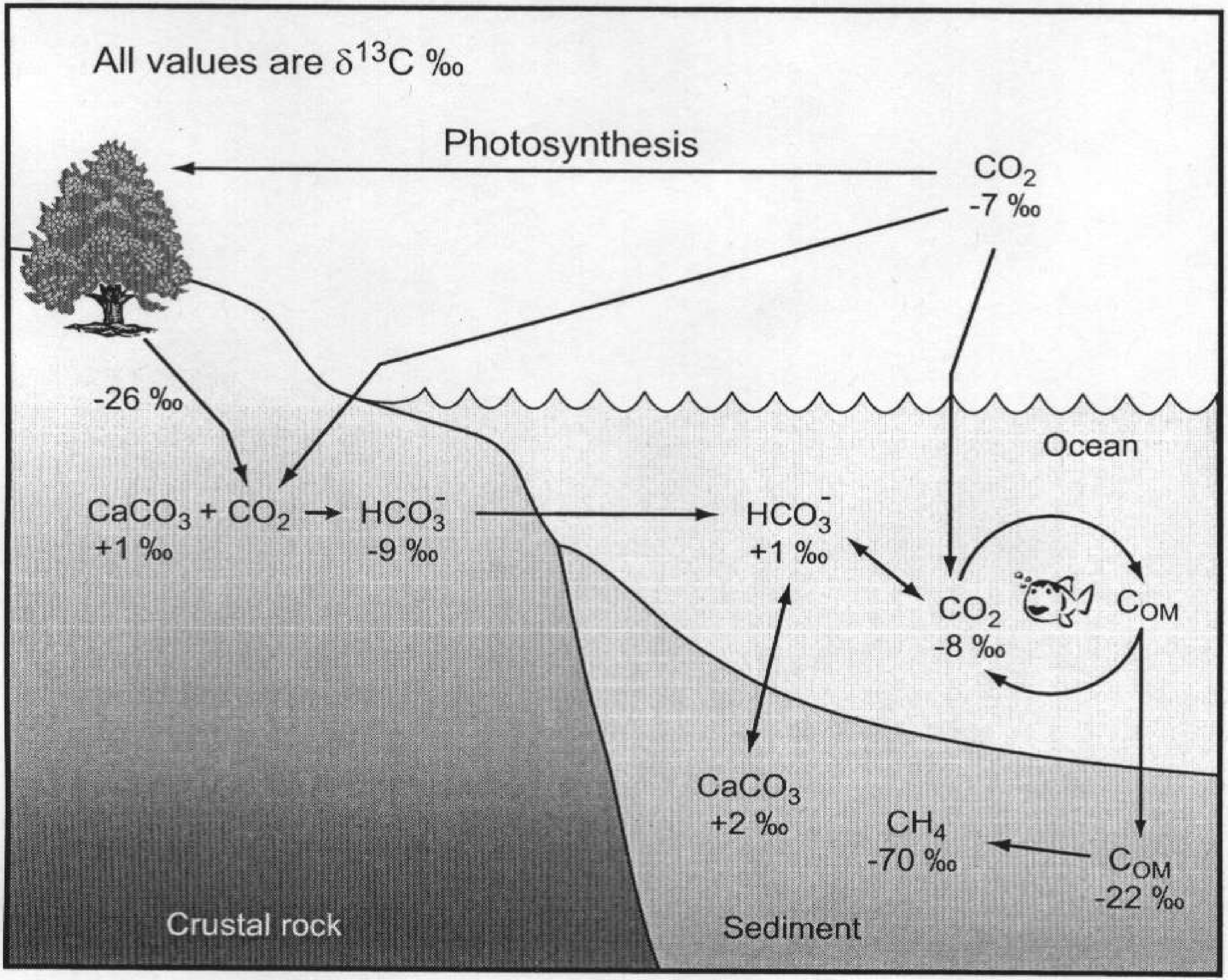
AND CONVERTS THE CO_2 TO ORGANIC MATTER

THIS PROCESS, IS USUALLY (BUT NOT ALWAYS)
DRIVEN BY SOLAR ENERGY,
IN A LOW TEMPERATURE
REDUCTION OF OXIDIZED CARBON,

PROCESSED PRIMARILY BY
PHOTOSYNTHETIC FIXATION OF CO_2
UTILIZING THE
CALVIN CYCLE

THE PRINCIPAL PATHWAYS OF AUTOTROPHIC CARBON ASSIMILATION ARE ACCOMPANIED BY MARKED FRACTIONATION OF THE STABLE CARBON ISOTOPES ^{12}C AND ^{13}C

“AN AUTOTROPH IS AN ORGANISM CAPABLE OF MAKING NUTRITIVE ORGANIC MOLECULES FROM INORGANIC SOURCES VIA PHOTOSYNTHESIS (INVOLVING LIGHT ENERGY) OR CHEMOSYTHESIS (INVOLVING CHEMICAL ENERGY)”

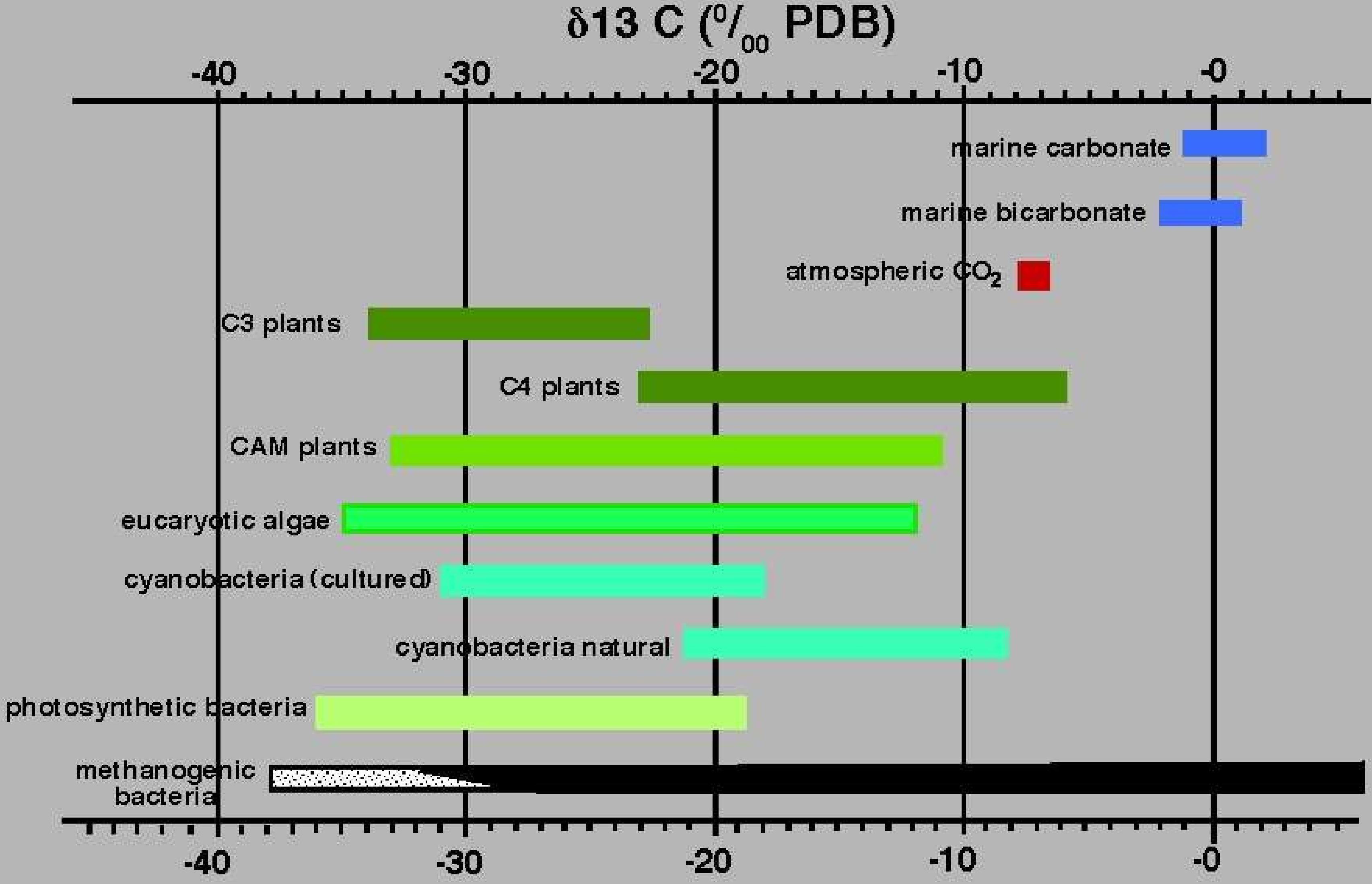


All values are $\delta^{13}C$ ‰

C3 organisms = plants such as beans, potatoes, rice, wheat

Crassulacean Acid Metabolism (CAM) (brown and green algae)

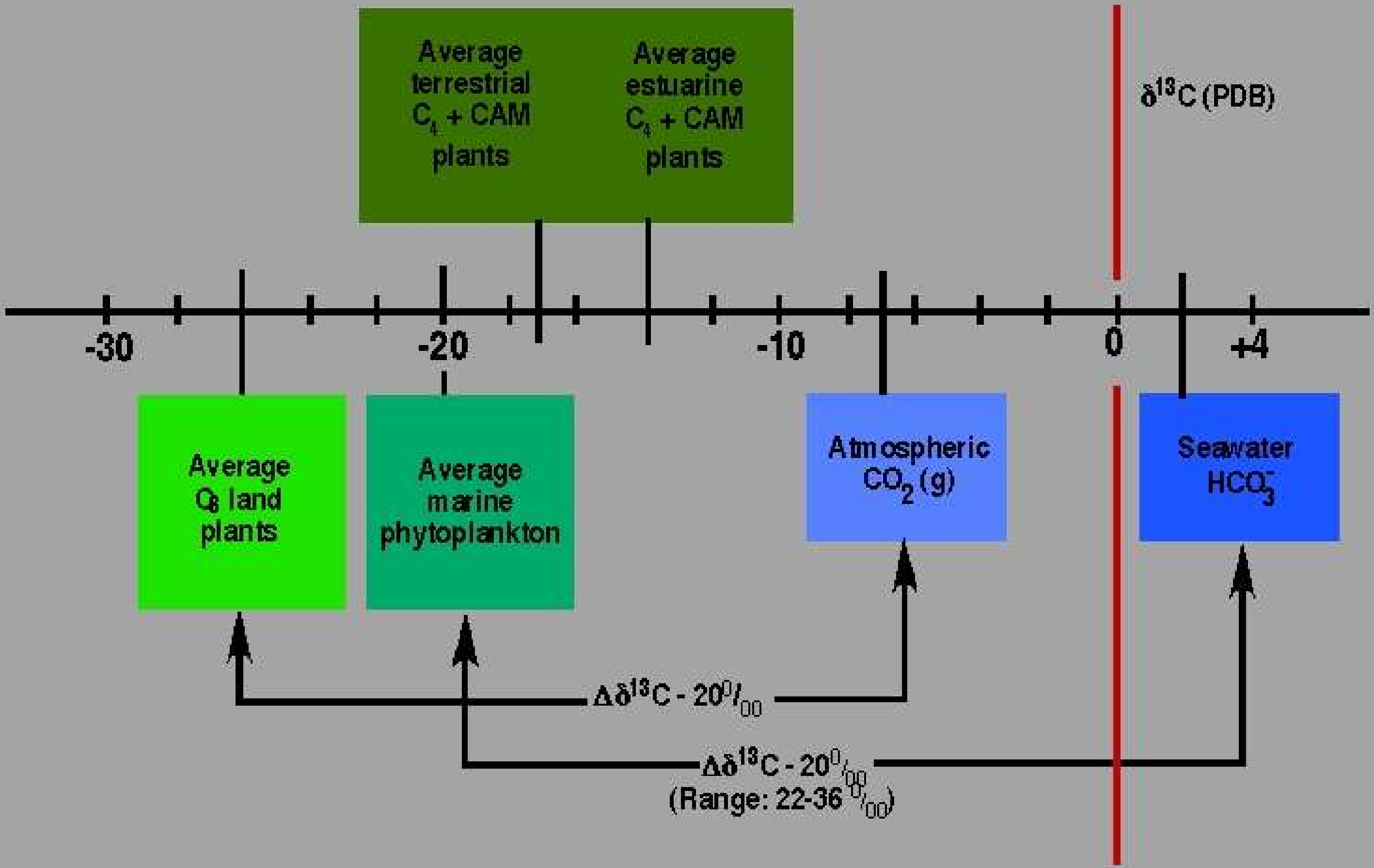
C4 organisms = trees, corn



Carbon isotope composition of extant higher plants, algae, and autotrophic prokaryotes compared with sedimentary carbonate, and enviromental reservoirs of oceanic bicarbonate & atmospheric CO_2

Schidlowski, Hayes & Kaplan, 1983

INFLUENCE OF CARBON SOURCES AND KINETIC FRACTIONATION ON THE AVERAGE ISOTOPIC COMPOSITION OF MARINE AND TERRESTRIAL PLANTS



Average terrestrial C_4 + CAM plants

Average estuarine C_4 + CAM plants

$\delta^{13}C$ (PDB)

Average C_3 land plants

Average marine phytoplankton

Atmospheric CO_2 (g)

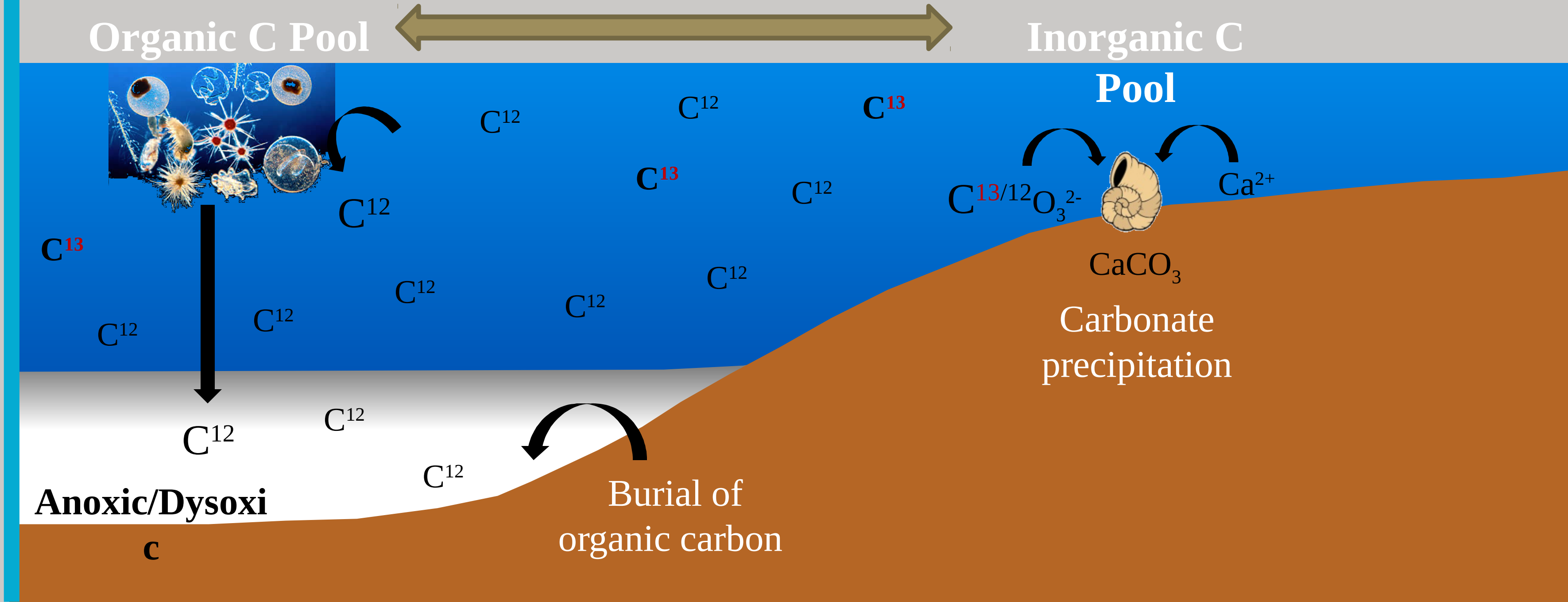
Seawater HCO_3^-

$\Delta\delta^{13}C$ - $20^0/_{00}$

$\Delta\delta^{13}C$ - $20^0/_{00}$
(Range: 22-36 $^0/_{00}$)

ISOTOPE BASICS

Steady-state, non-equilibrium carbon isotope fractionation between the Total Dissolved Carbon (TDC) in the shallow and deep ocean due to high biological activity in the near-surface photic zone of the ocean. Photosynthesizing organisms preferentially incorporate ^{12}C in their tissues



Organic C Pool

Inorganic C Pool

C^{12} C^{12} **C^{13}**

C^{13} C^{12} C^{12}

C^{13} C^{12} C^{12} C^{12} C^{12} C^{12}

$C^{13/12}O_3^{2-}$

Ca^{2+}

$CaCO_3$

Carbonate precipitation

C^{12} C^{12} C^{12}

Anoxic/Dysoxic

Burial of organic carbon

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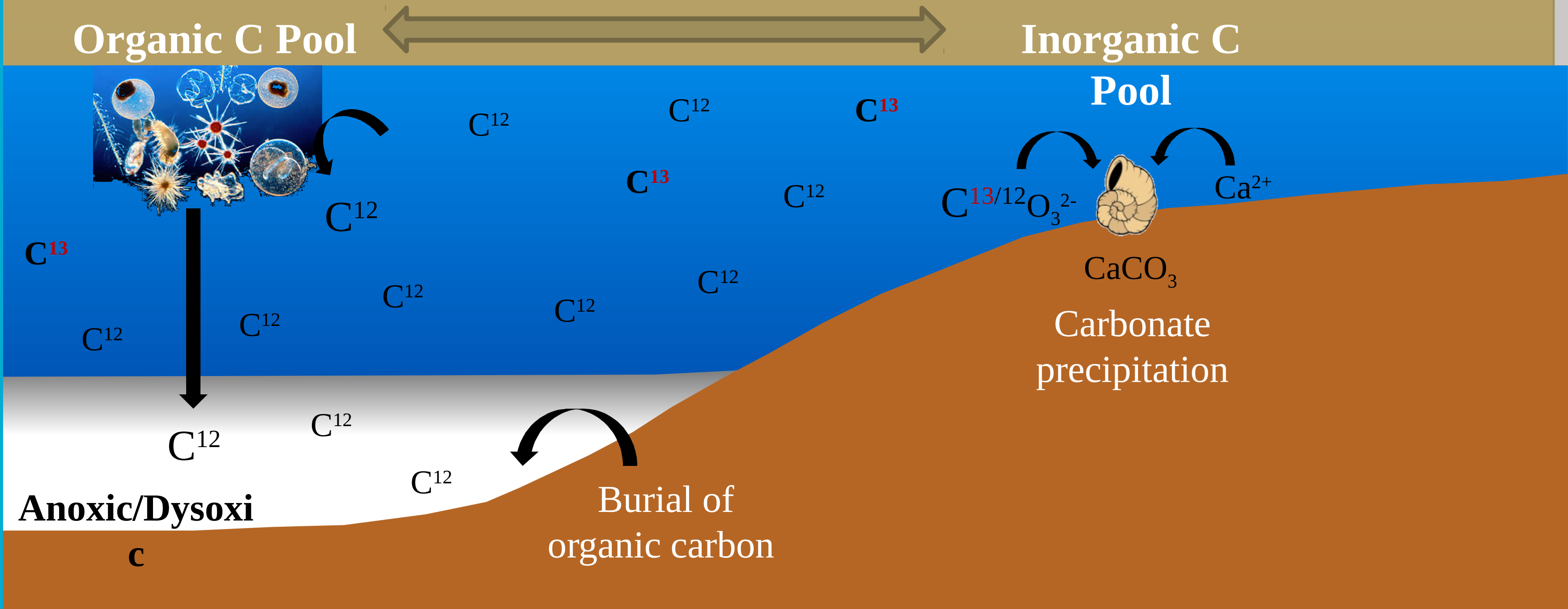
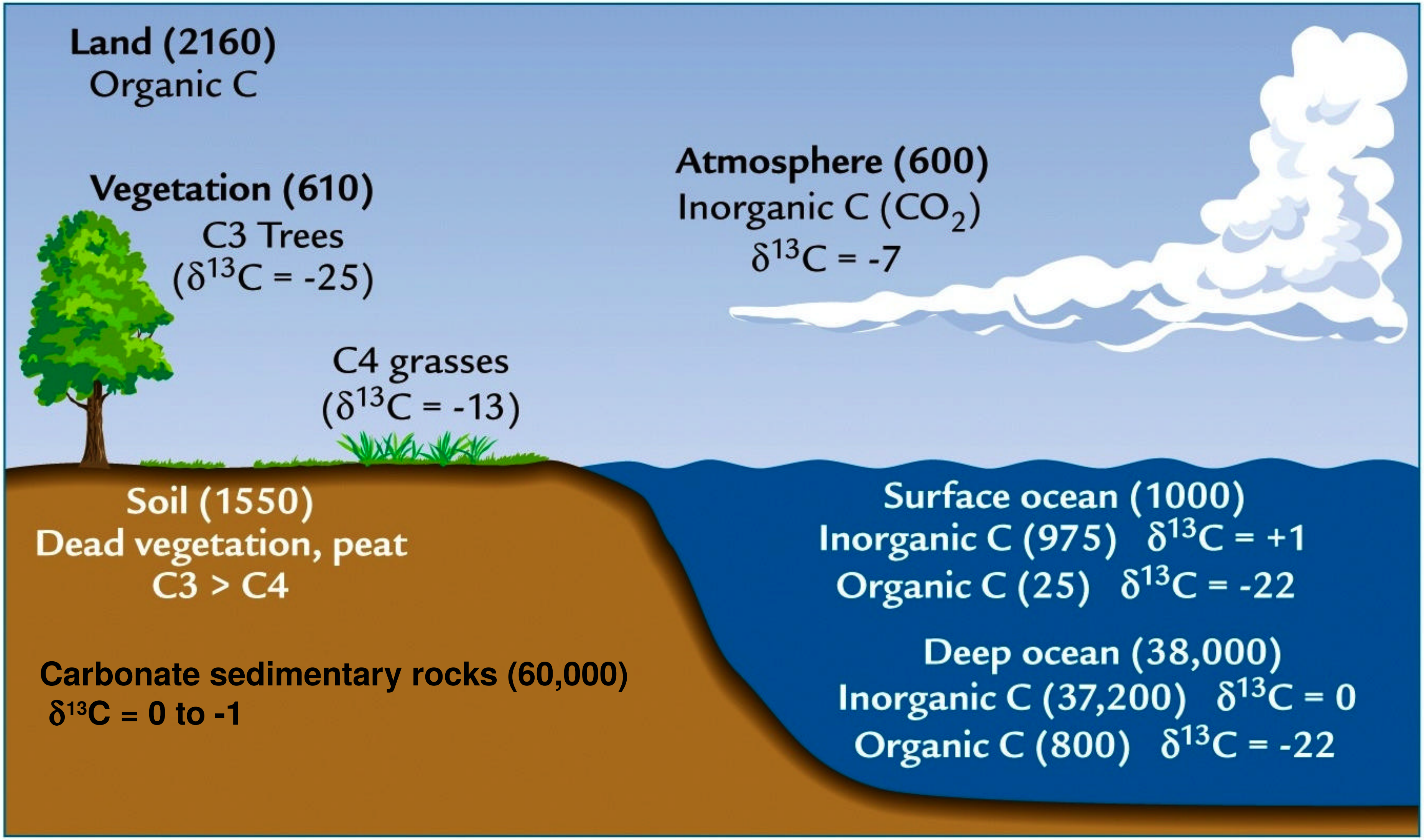
This leaves more ^{13}C in the remaining water (surface) and a greater amount of ^{12}C in the bottom deposits (1-2%)



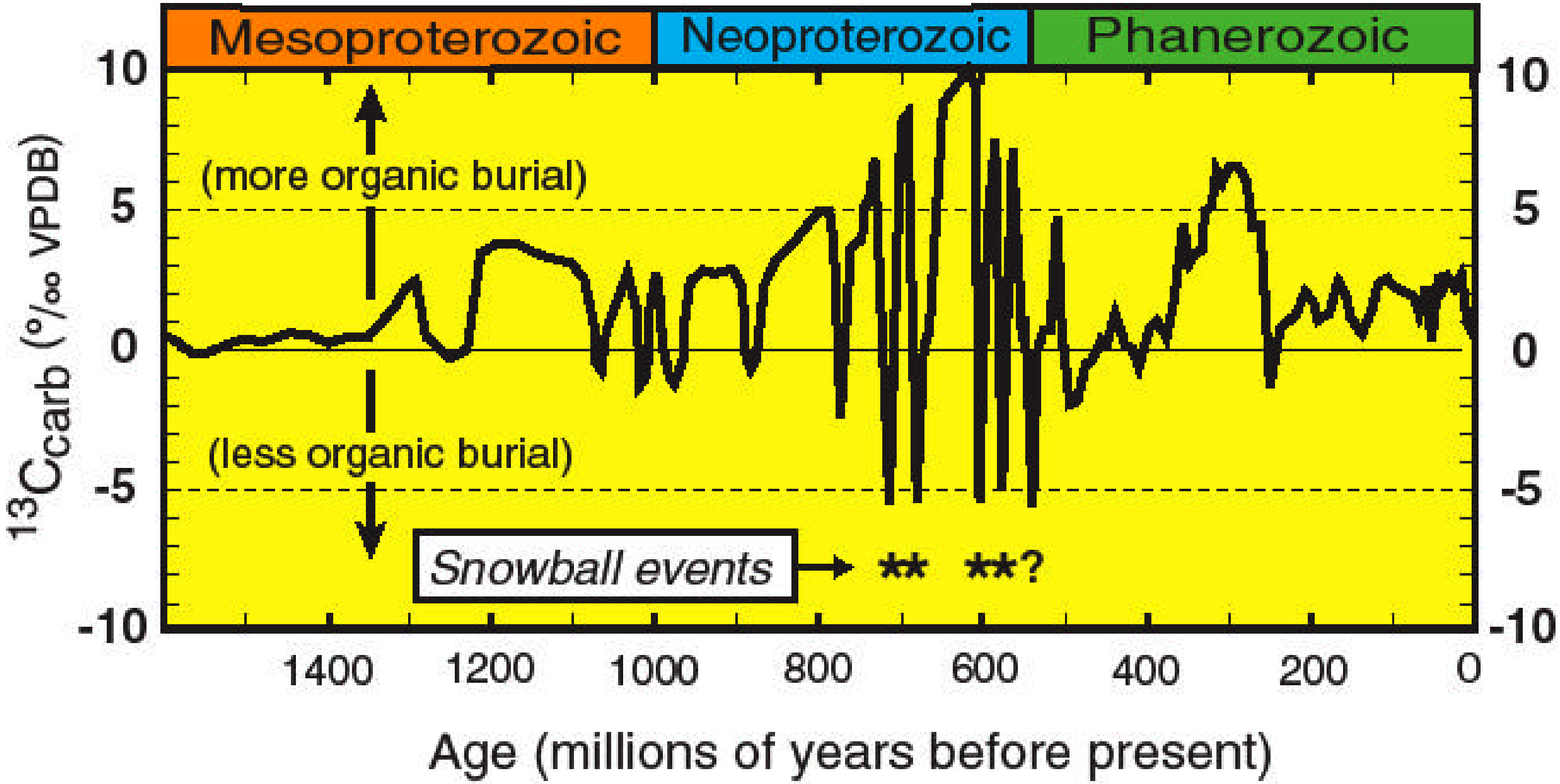
Residence time & reservoirs

Size and $\delta^{13}C$ (vs PDB) of Earth's Carbon Reservoirs



Carbon cycle showing approximate amounts, fluxes and $\delta^{13}C$ values of different reservoirs. Abundances are given in (10^{15}g)

δ^{13}C in the Carbonate Rock Record

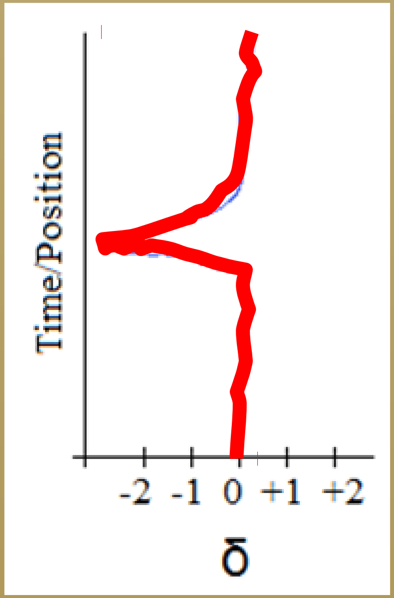


Secular variation in carbon isotopic composition of shallow marine carbonates over the last 1600 million years (adapted from Kaufman, 1997; Kah et al., 1999).

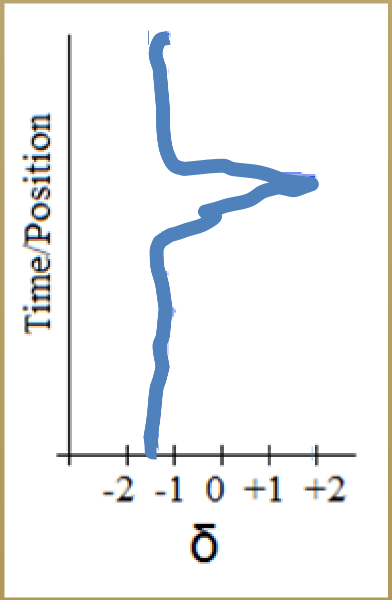
$\delta^{13}C$ is sensitive to paleoenvironmental changes

- biological productivity
- ocean circulation
- organic carbon burial

- Decreased biological productivity
- Increased mixing or upwelling
- Increased weathering of organic carbon

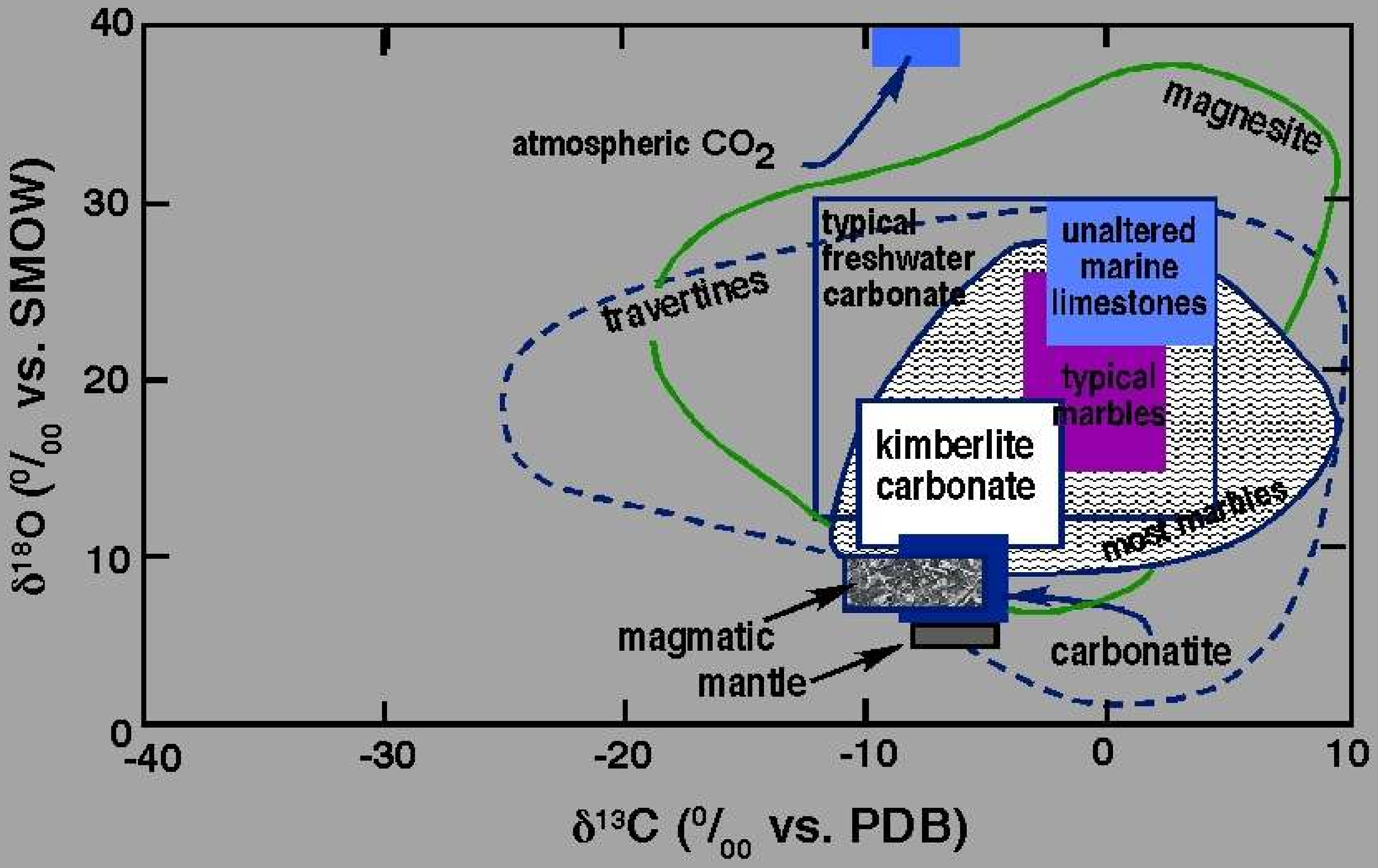


Negative shift =
Depleted in ^{13}C



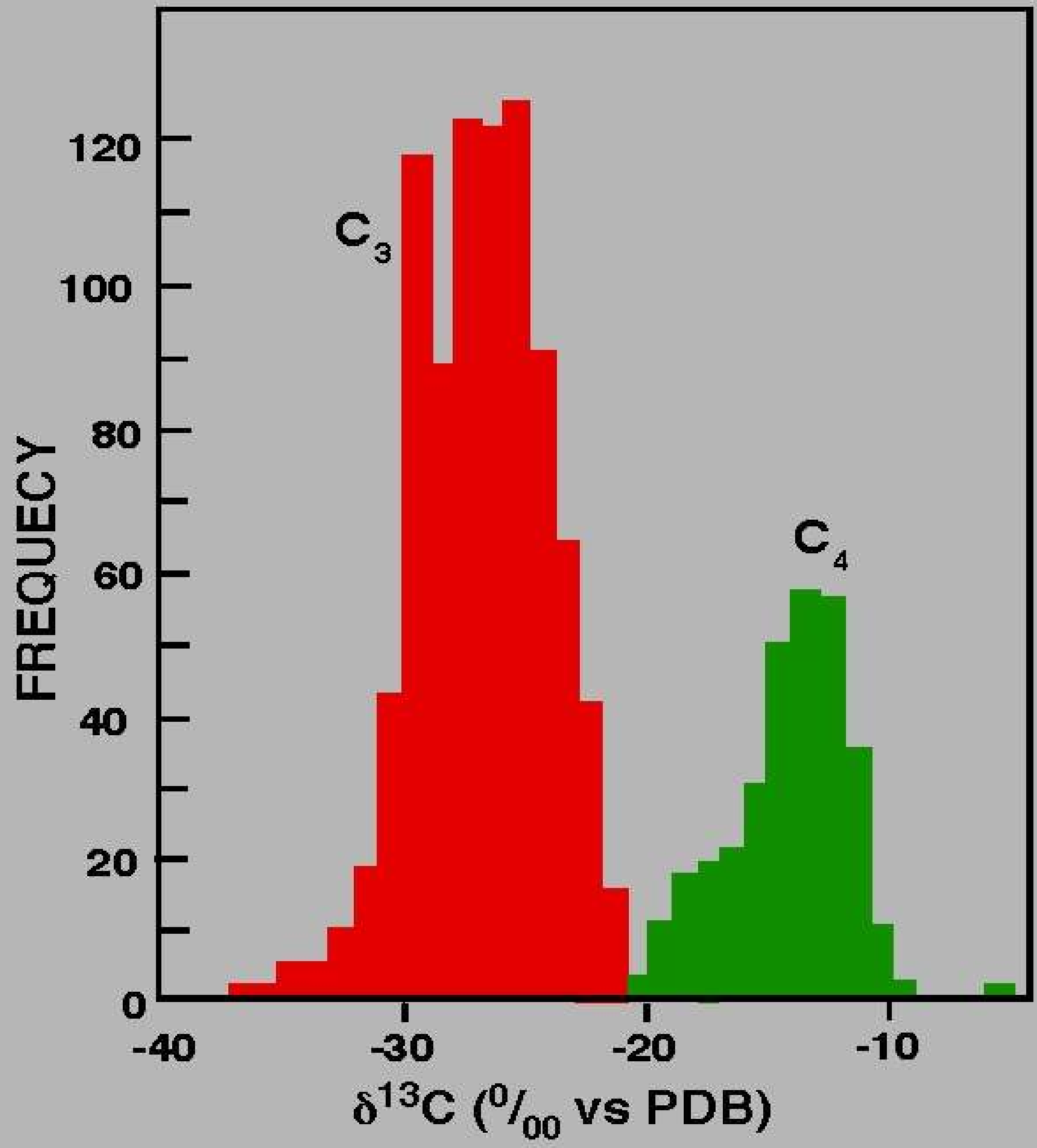
Positive shift =
Enriched in ^{13}C

- Increased biological productivity
- Decreased ocean circulation
- Increased organic carbon burial

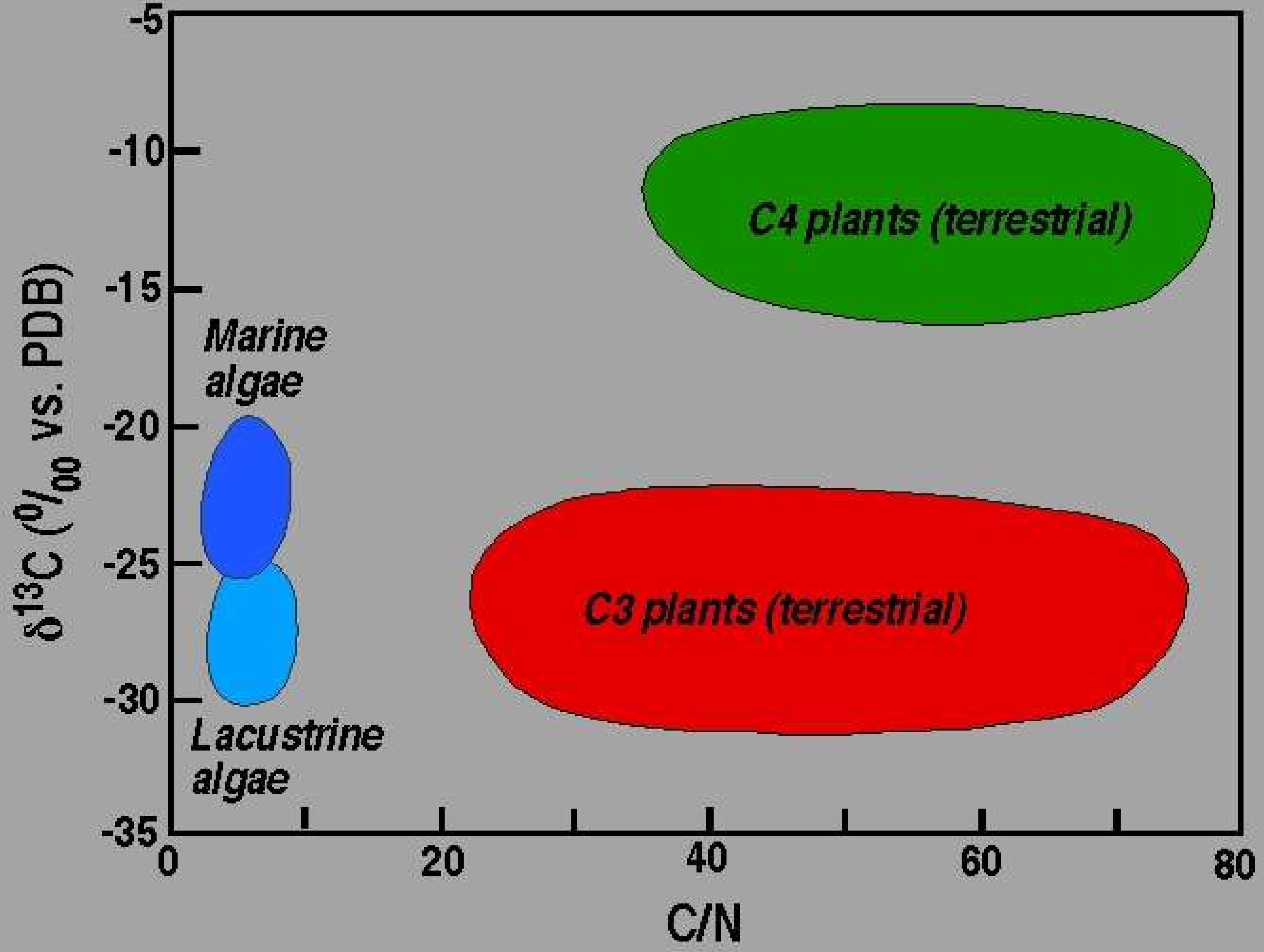


Sharp, 2007, Fig 7.2

EXPLAIN PLANT TYPES

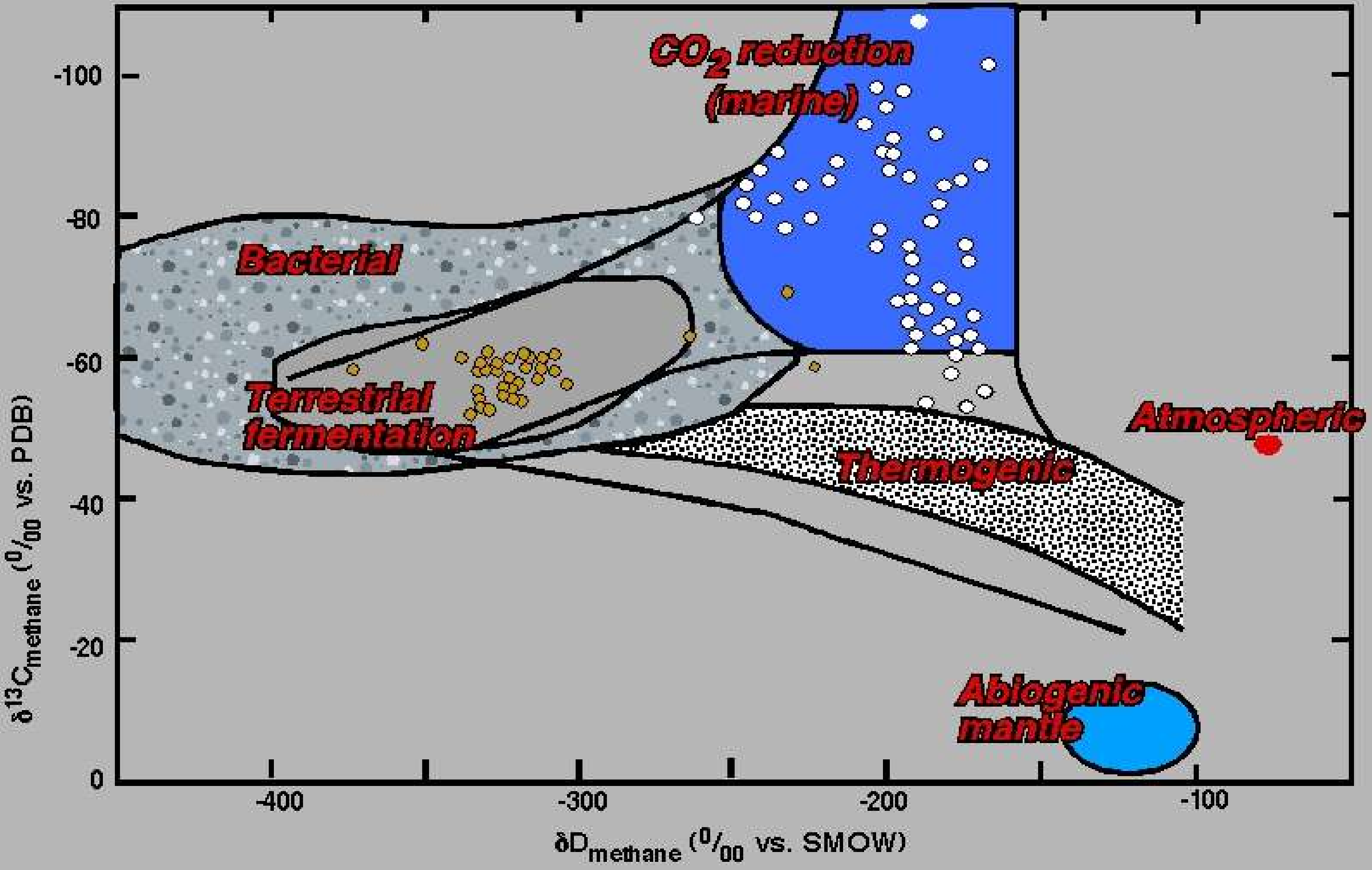


$\delta^{13}C$ values of C_3 and C_4 terrestrial plants. The difference of $13^0/_{00}$ between the two groups makes for unambiguous identification.



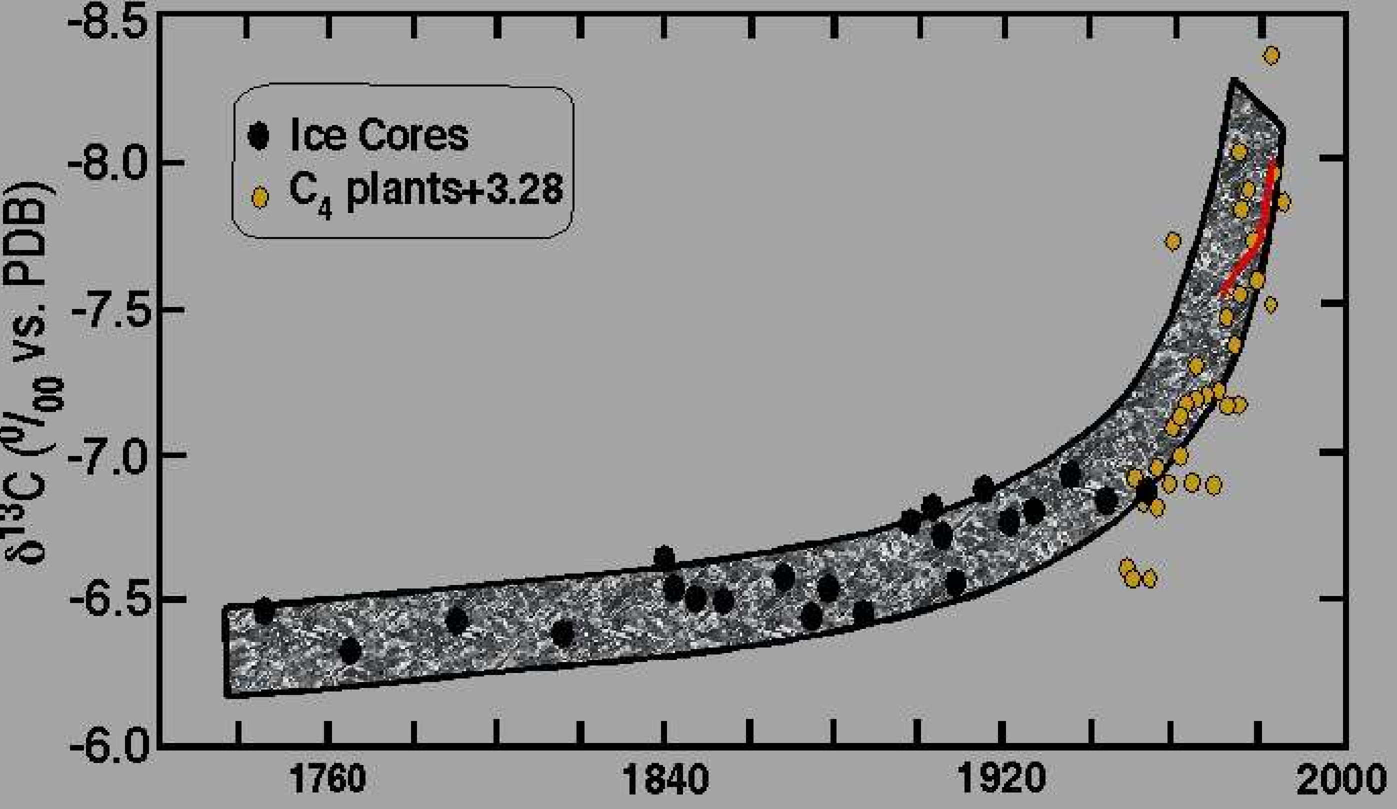
C/N ratios vs $\delta^{13}C$values of organic matter. The absence of cellulose in aquatic plants and algae lead to much lower C/N ratios than those in terrestrial plants. Minor diagenesis will not appreciably affect either C/N or isotope ratios.

Sharp, 2007



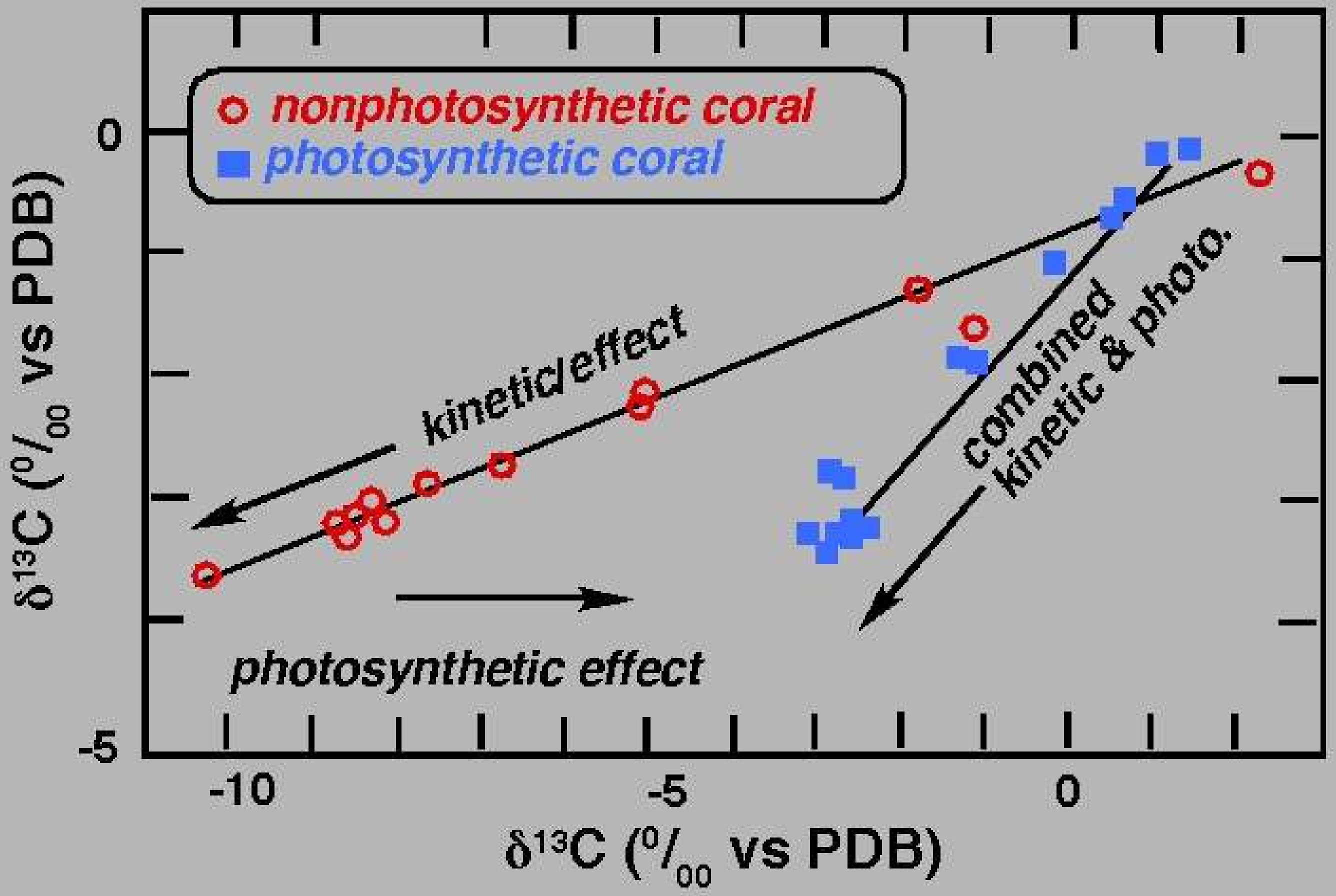
Combined carbon-hydrogen isotope plot of methane. Using combined carbon and hydrogen isotope ratios, formations from terrestrial fermentation, marine CO_2 reduction, and thermal cracking can easily be distinguished.

Sharp, 2007



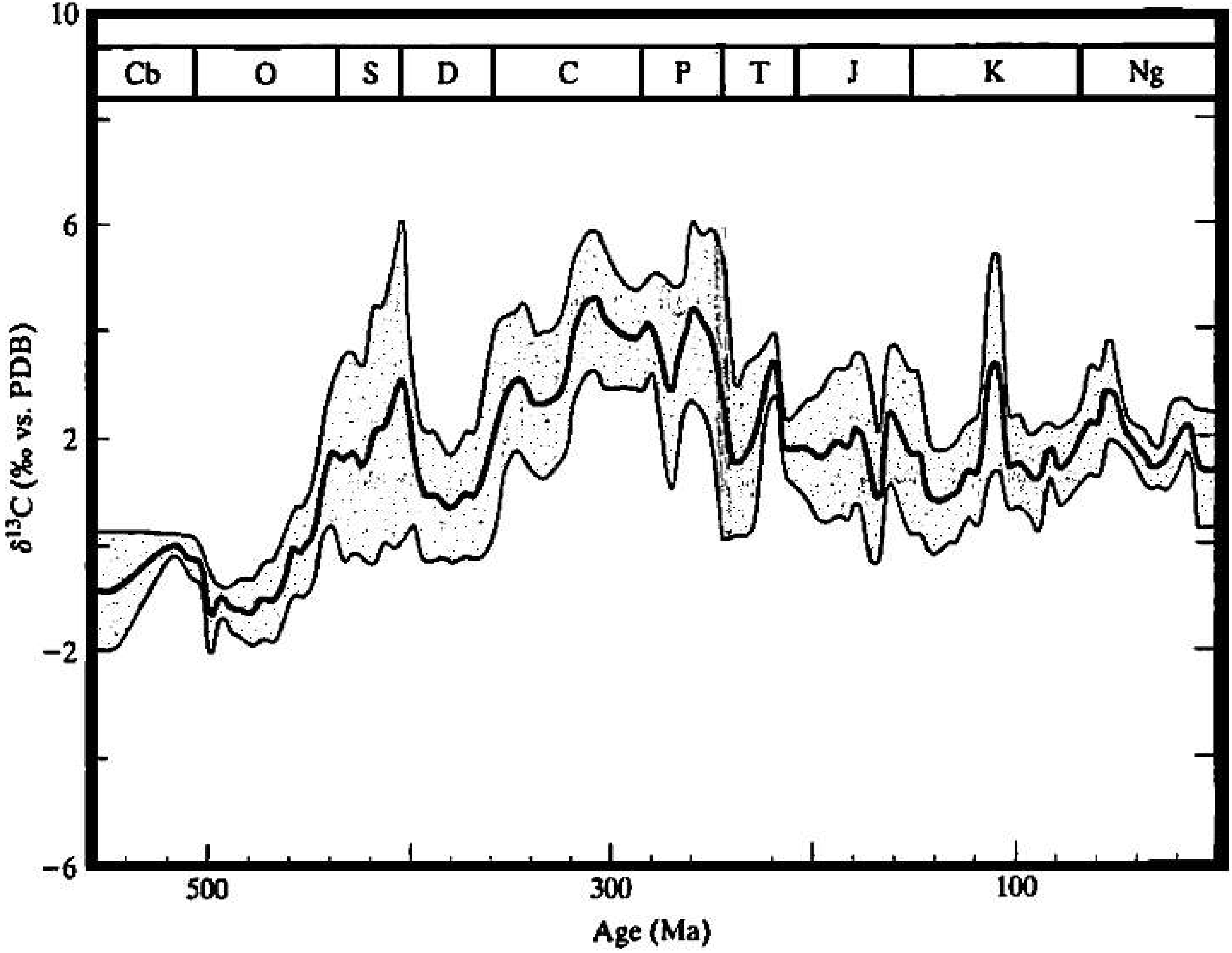
Variations in $\delta^{13}C$ value of atmospheric CO_2 as a function of age. Data are from direct measurements of atmospheric CO_2 (red line starting in 1970); ice-core air inclusions (black circles); and measured $\delta^{13}C$ values of C_4 maize (yellow circles).

Sharp, 2007

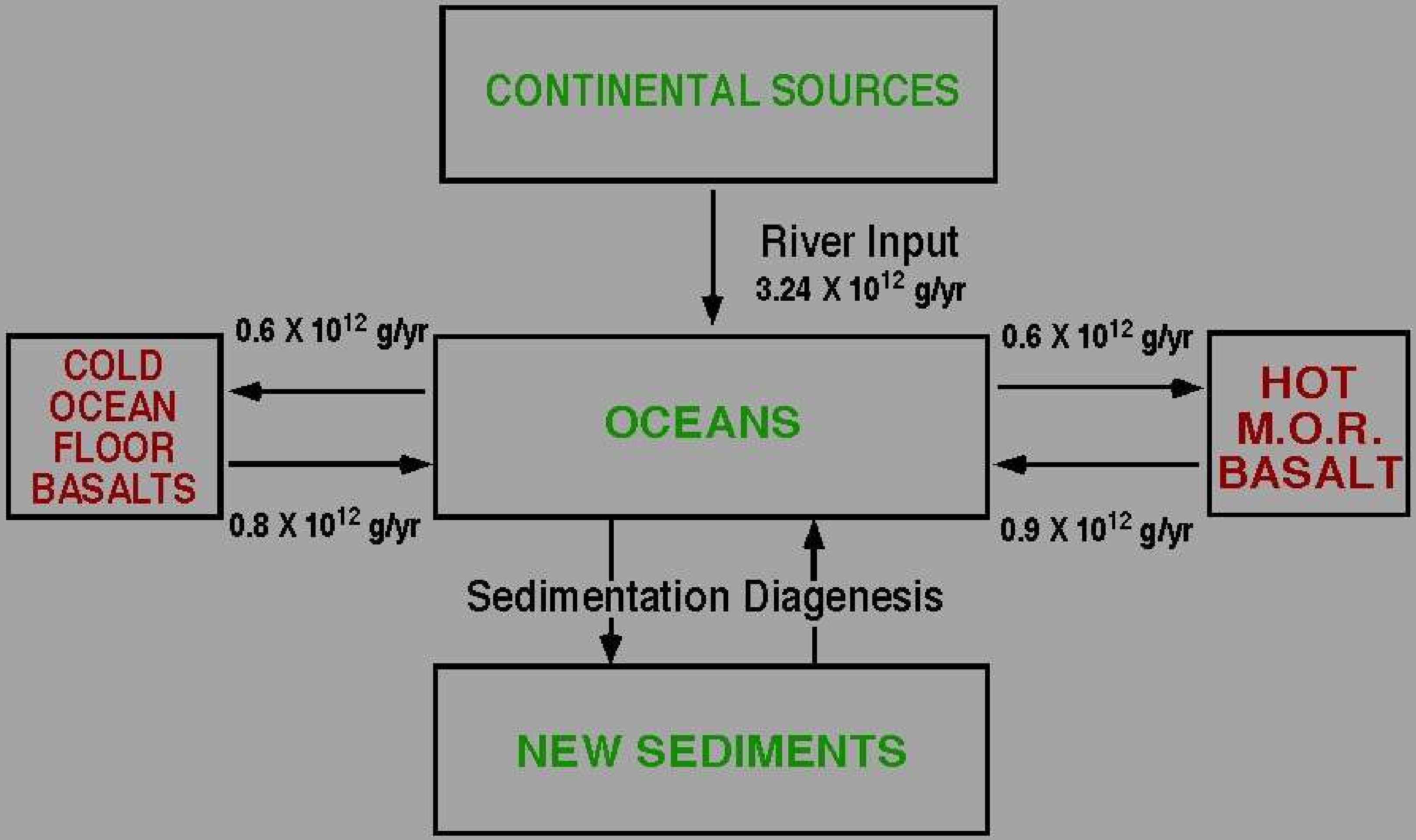


Stable isotope data for the photosynthetic coral *Pavona clavus* (squares) and the nonphotosynthetic coral *Tubastrea sp* (circles). The covariation of $\delta^{18}O$ and $\delta^{13}C$ values for the ahermatypic coral is the normal *kinetic* relation and the higher $\delta^{13}C$ values for the photosynthesizing coral is explained by metabolic relation arising from preferential incorporation of ^{12}C during photosynthesis, causing and elevation of $\delta^{13}C$ values of remaining inorganic C.

from McConnaughey, 1989



Secular variations of $\delta^{13}C$ values of marine carbonates. Data only from low Mg carbonate shells. Shaded area represents range of uncertainty (after Veizer et al., 1999)



CONTINENTAL SOURCES

River Input
3.24 X 10^{12} g/yr

COLD OCEAN FLOOR BASALTS

0.6 X 10^{12} g/yr

0.8 X 10^{12} g/yr

OCEANS

0.6 X 10^{12} g/yr

0.9 X 10^{12} g/yr

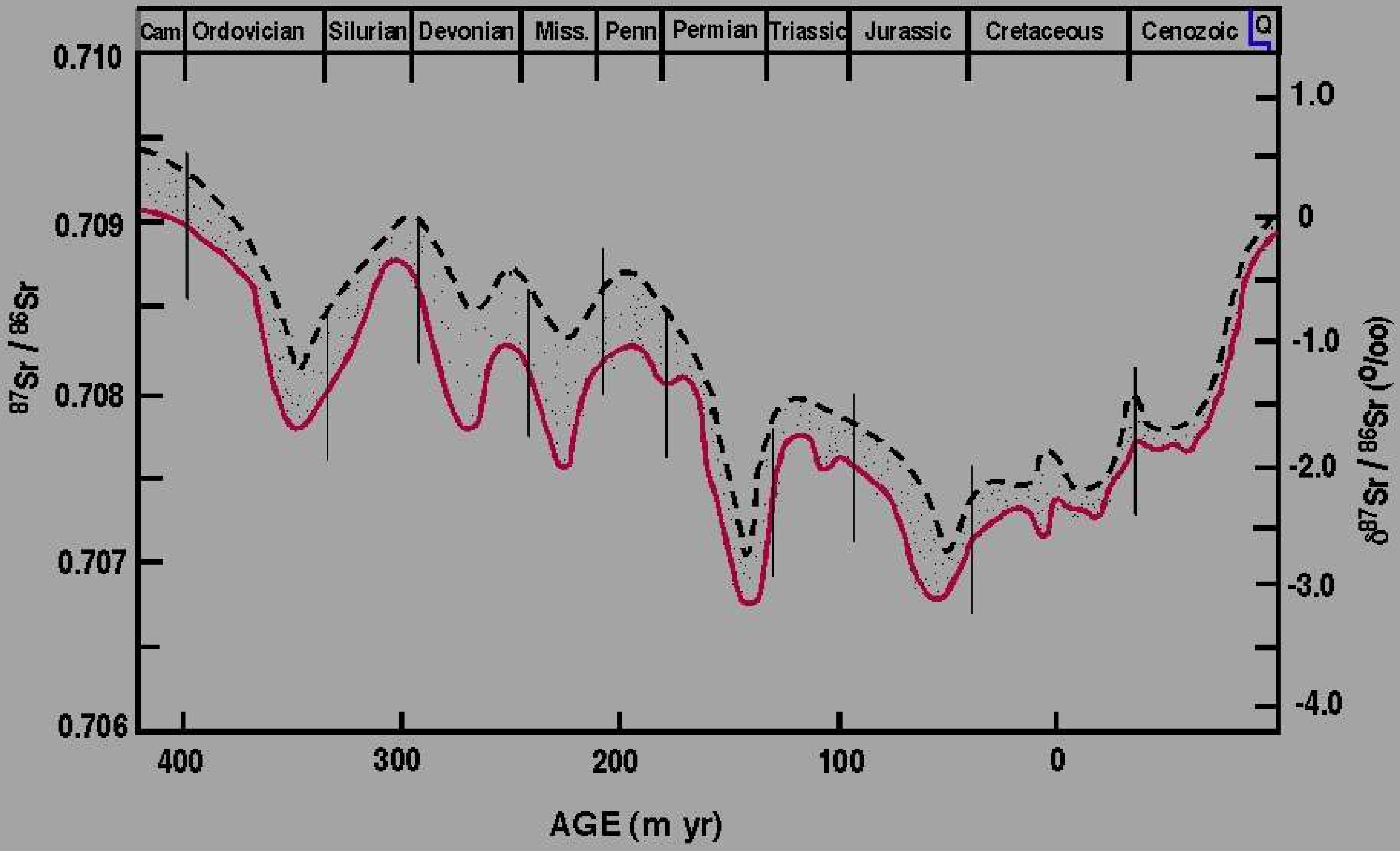
HOT M.O.R. BASALT

Sedimentation Diagenesis

NEW SEDIMENTS

THE GEOCHEMICAL CYCLE OF STRONTIUM
(modified from Holland, 1984)

Schlanger, 1988



Variations in the $^{87}Sr/^{86}Sr$ ratio of seawater through Phanerozoic time.

STRONTIUM ISOTOPES

Why and how it is used in estimating stratigraphic position of carbonates and evaporites

Review by B.C. Schreiber

ONE OF THE MOST USEFUL,
CONSERVATIVE, AND STABLE ELEMENTS
FOR
ISOTOPIC STUDY
IN SEDIMENTARY ROCKS
(CARBONATES AND EVAPORITES)

IT HAS BEEN TREATED AS A GEOLOGICAL
"TRACER"

RESIDENCE TIME OF STRONTIUM IN THE OCEANS

>2 M.Y.

MIXING TIME OF STRONTIUM IN THE OCEANS

~103 YEARS

BACKGROUND

During fractional crystallization, Sr tends to be come concentrated in the first minerals to crystallize, leaving Rb in the liquid phase.
Hence, the Rb/Sr ratio in residual magma may increase over time, resulting in rocks with increasing Rb/Sr ratios with increasing differentiation.

Highest ratios occur in pegmatites. Typically, Rb/Sr increases in the order plagioclase, hornblende, K-feldspar, biotite, muscovite. Therefore, given sufficient time for significant production (ingrowth) of radiogenic ^{87}Sr, measured ^{87}Sr/^{86}Sr values will be different in the minerals, increasing in the same order.

The Rb-Sr dating method has been used extensively in dating rocks. If the initial amount of Sr is known or can be extrapolated, the age can be determined by measurement of the Rb and Sr concentrations and ^{87}Sr/^{86}Sr ratio.

The dates indicate the true age of the minerals **only** if the rocks have not been subsequently altered.

4 stable
naturally occurring isotopes

^{84}Sr (0.56%), ^{86}Sr (9.86%), ^{87}Sr (7.0%) and ^{88}Sr (82.58%)

Strontium
is present as a ubiquitous minor element
in the crust of the Earth –

Strontium is present as a ubiquitous minor element in the crust of the Earth –

Present in many rock types.

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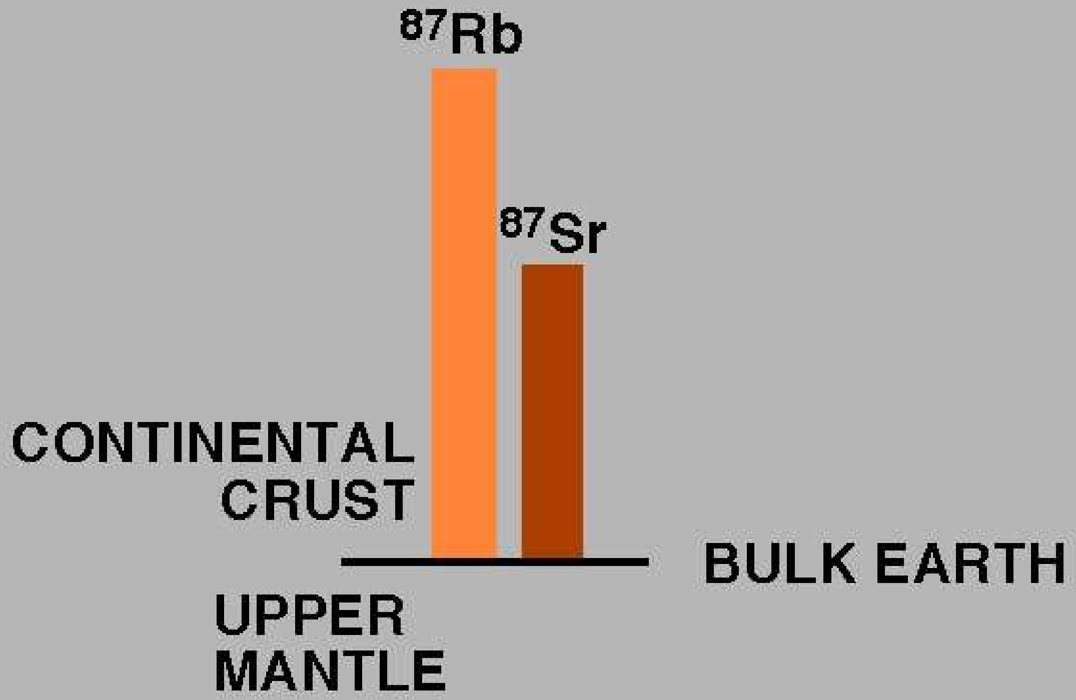
Present in many rock types.

Typically found in concentrations of a few hundred parts per million

^{87}Sr

^{87}Rb

half-life of 48,800,000 years



FRACTIONATION OF Rb/Sr BETWEEN UPPER MANTLE AND CONTINENTAL CRUST

Elderfield, 1986