Three oxygen isotopes in nature

^{16}O 99.76%

^{17}O 0.04%

^{18}O 0.2%

For isotope analyses we use $^{18}O/^{16}O$

Stable Isotopes in Foraminifers

F.J. Sierro

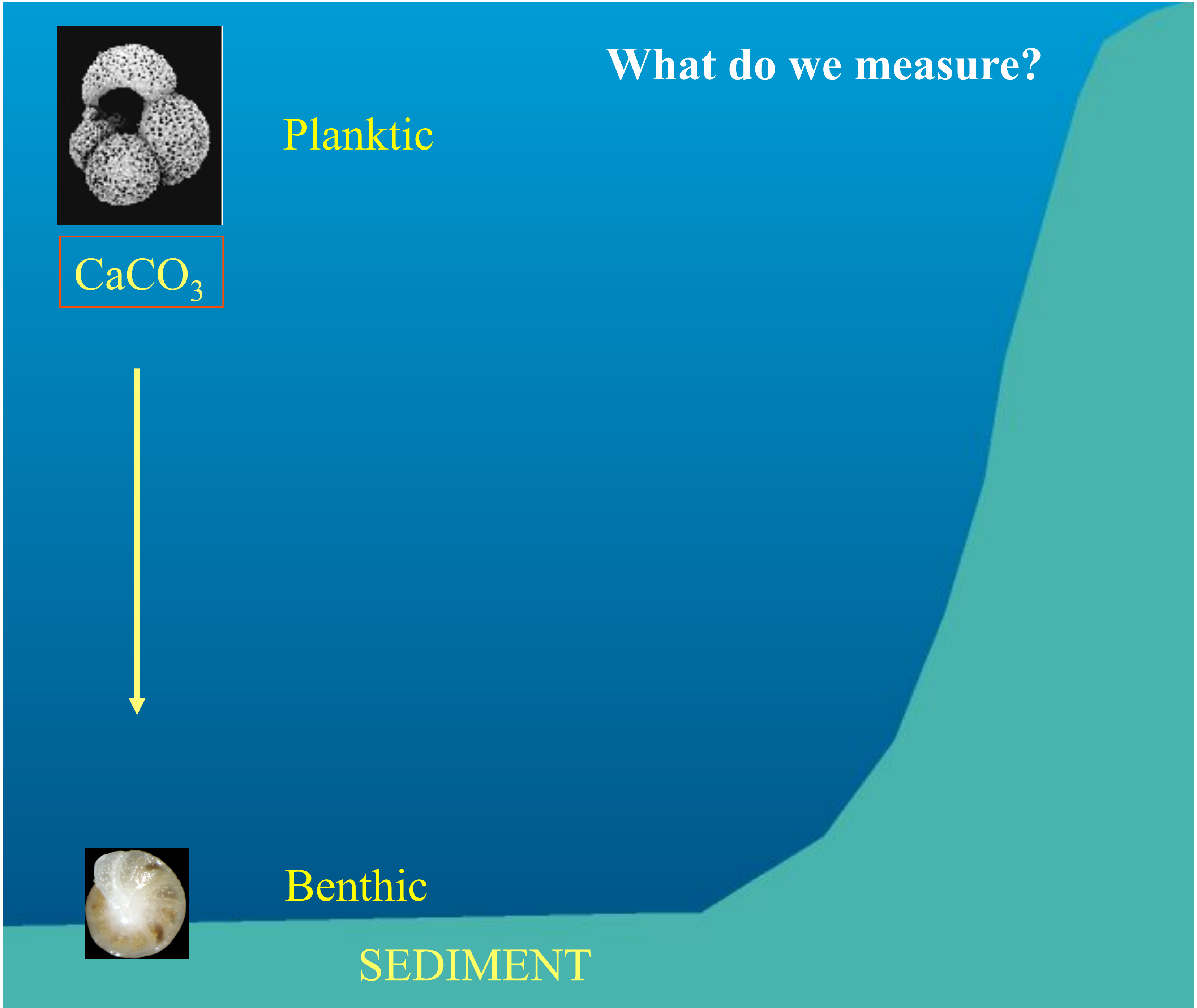
δ notation

$$\delta\, pdb^{18}O = \frac{{}^{18}O/{}^{16}O_{sample} - {}^{18}O/{}^{16}O_{standard}}{{}^{18}O/{}^{16}O_{standard}} \times 1000$$

$\delta\, {}^{18}O = >0$ Enrichment in the heavy isotope relative to the standard

$\delta\, {}^{18}O = <0$ Depletion in the heavy isotope relative to the standard

Pdb = Pee Dee Belemnite *Belemnitella americana*

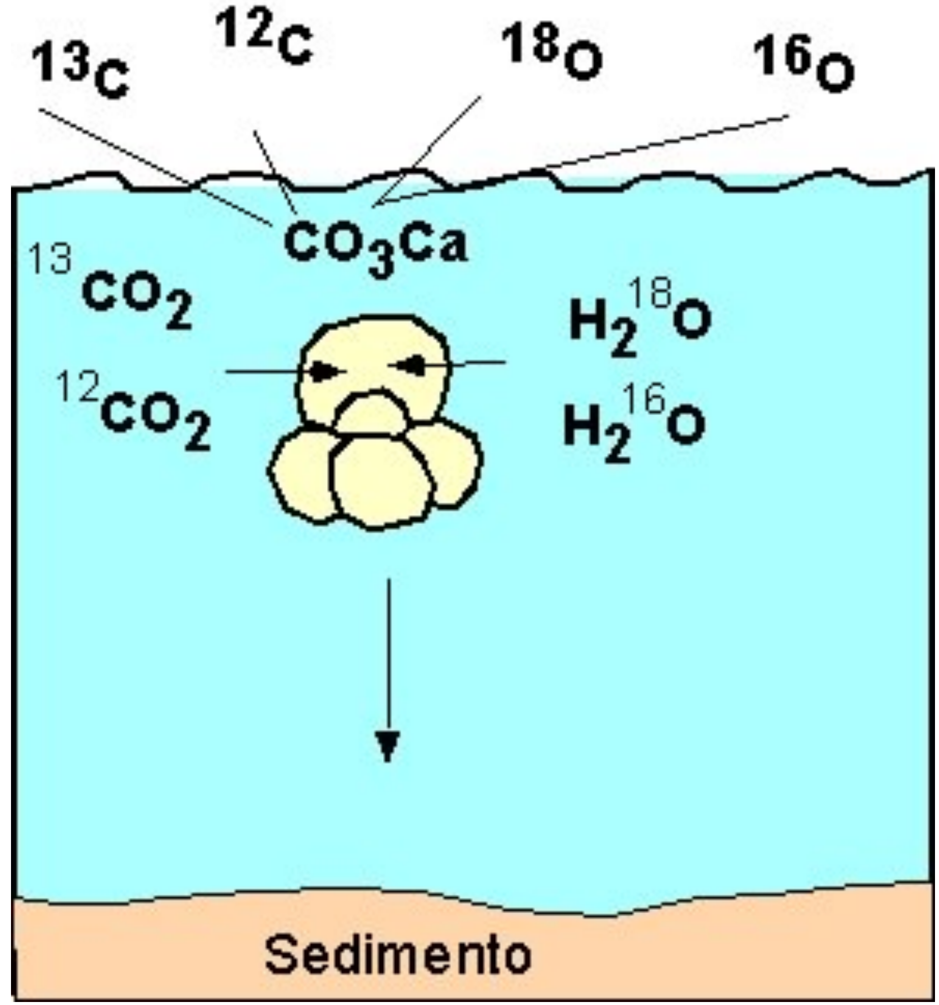

What do we measure?
Planktic
$CaCO_3$
Benthic
SEDIMENT

Factors that influence the isotope composition of Foraminifers

1: $\delta^{18}O$ of seawater: Ice volume (global effect)
Hydrologic cycle

2: Calcification temperature

It is assumed that foraminifers precipitate its calcite shell in isotope equilibrium with seawater $\delta^{18}O$



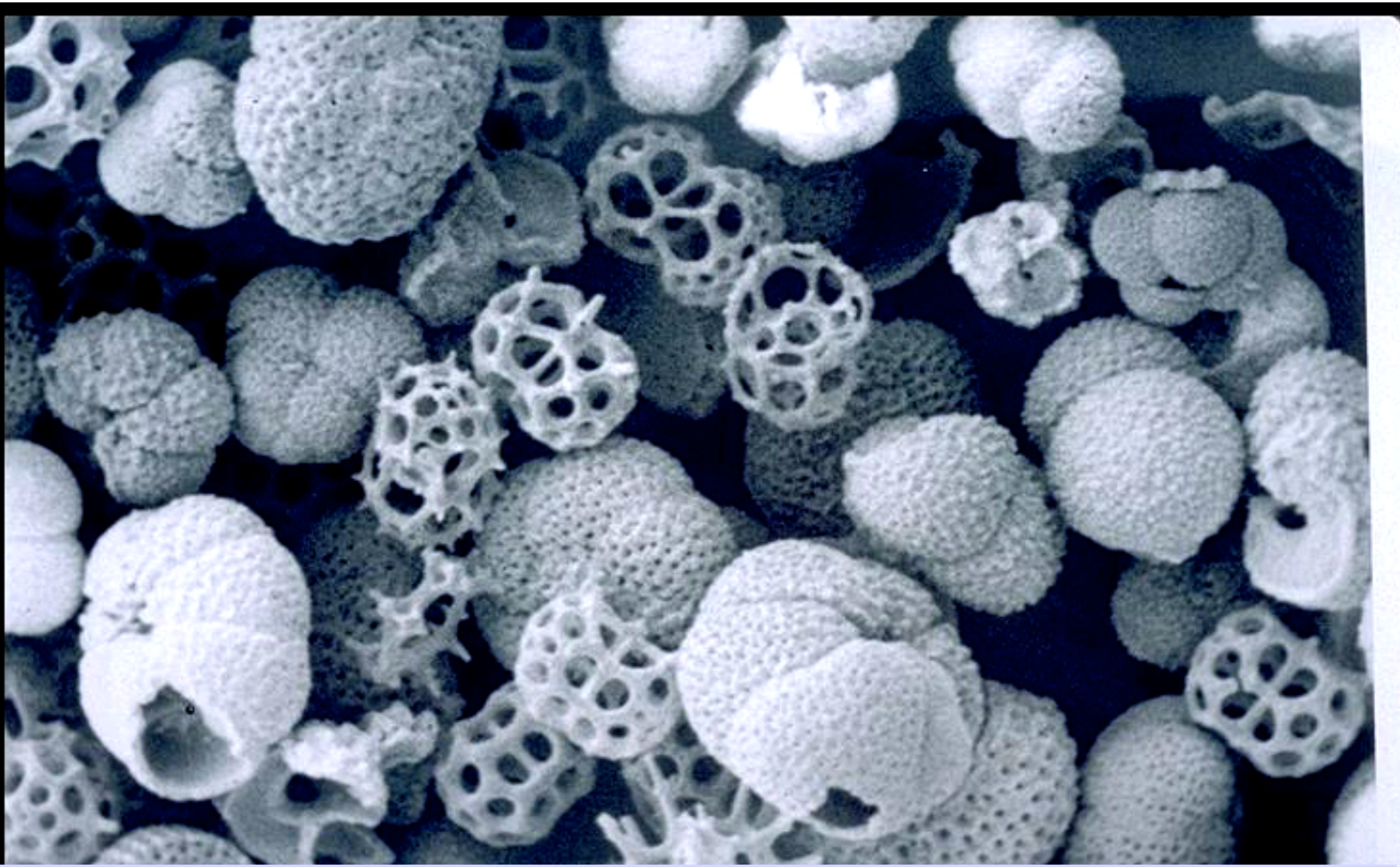
Deviations from equilibrium $\delta^{18}O$ in foraminifer calcite

Ontogenetic effect. $\delta^{18}O$ increase from juvenile chambers to adult chambers

Symbiont photosinthesis. $\delta^{18}O$ decrease for increasing irradiance

Carbonate ion concentration. $\delta^{18}O$ in foraminifers decreases with increasing $CO3^{2-}$

Gametogenic calcite. Some foraminifers precipitate a calcite crust during gametogenesis wich is enriched in the heavy isotope



Foraminifers calcify in oxygen isotope equilibrium with seawater

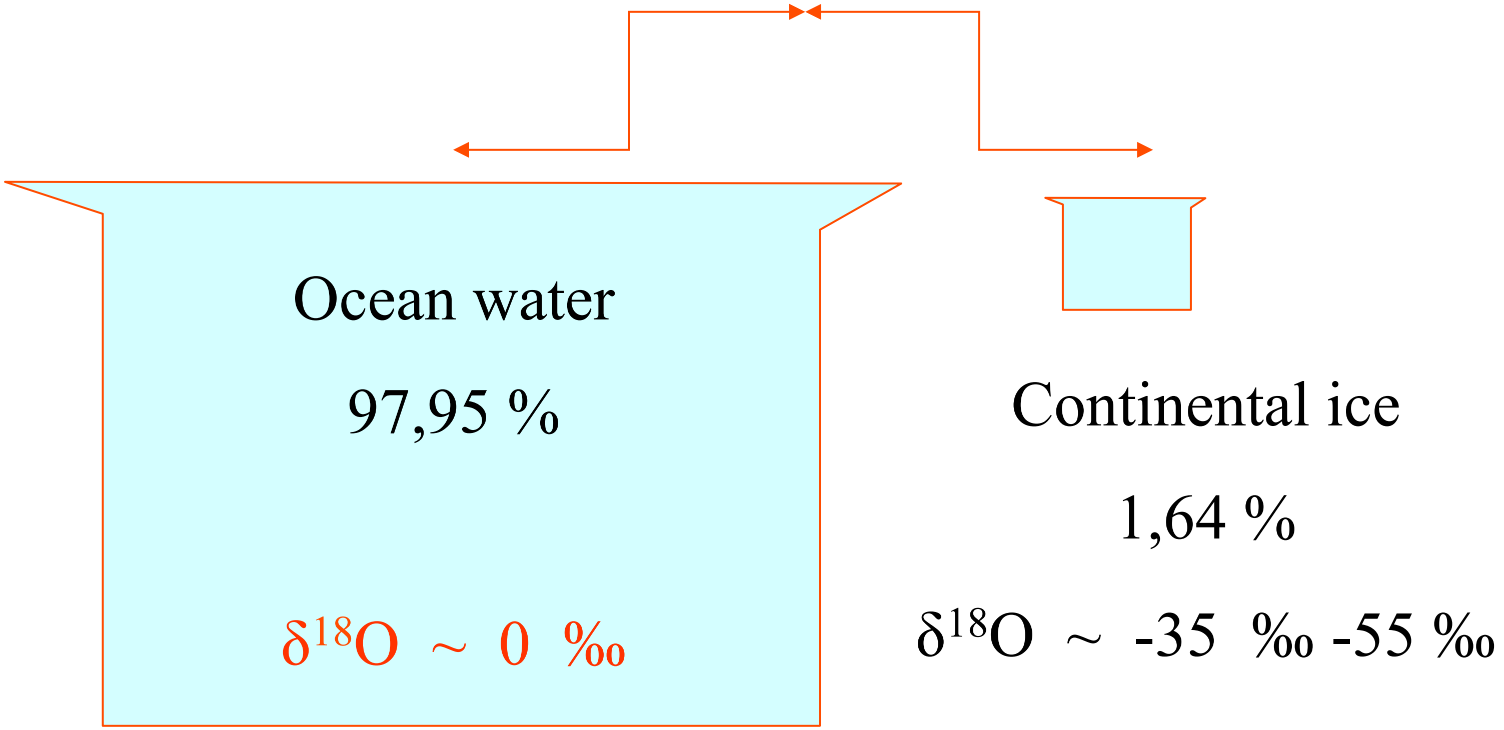
The water cycle on Earth: Water Reservoirs

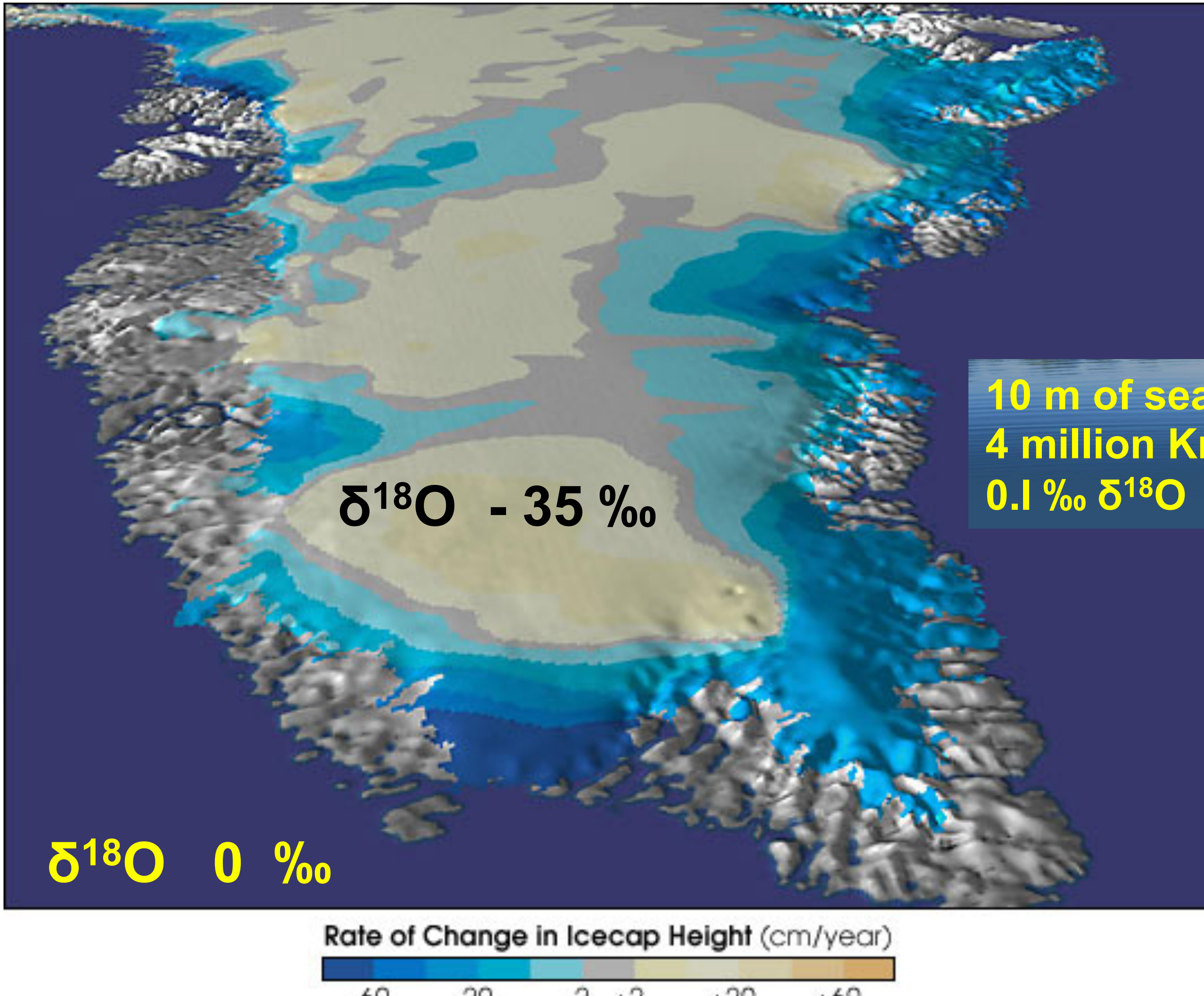
Ocean: 98.95%	$\delta^{18}O$ **0 ‰**
Ice sheets: 1.64%	$\delta^{18}O$ **-35 ‰** to **-55 ‰**
Groundwaters: 0.364%	$\delta^{18}O$ variable, usually negative
Rivers and lakes: 0.036%	$\delta^{18}O$ variable, usually negative

Ice volume effect

Transfer of water from the Ocean to the continent increase the $\delta^{18}O$ of seawater

Melting of icesheets decrease the average $\delta^{18}O$ of seawater

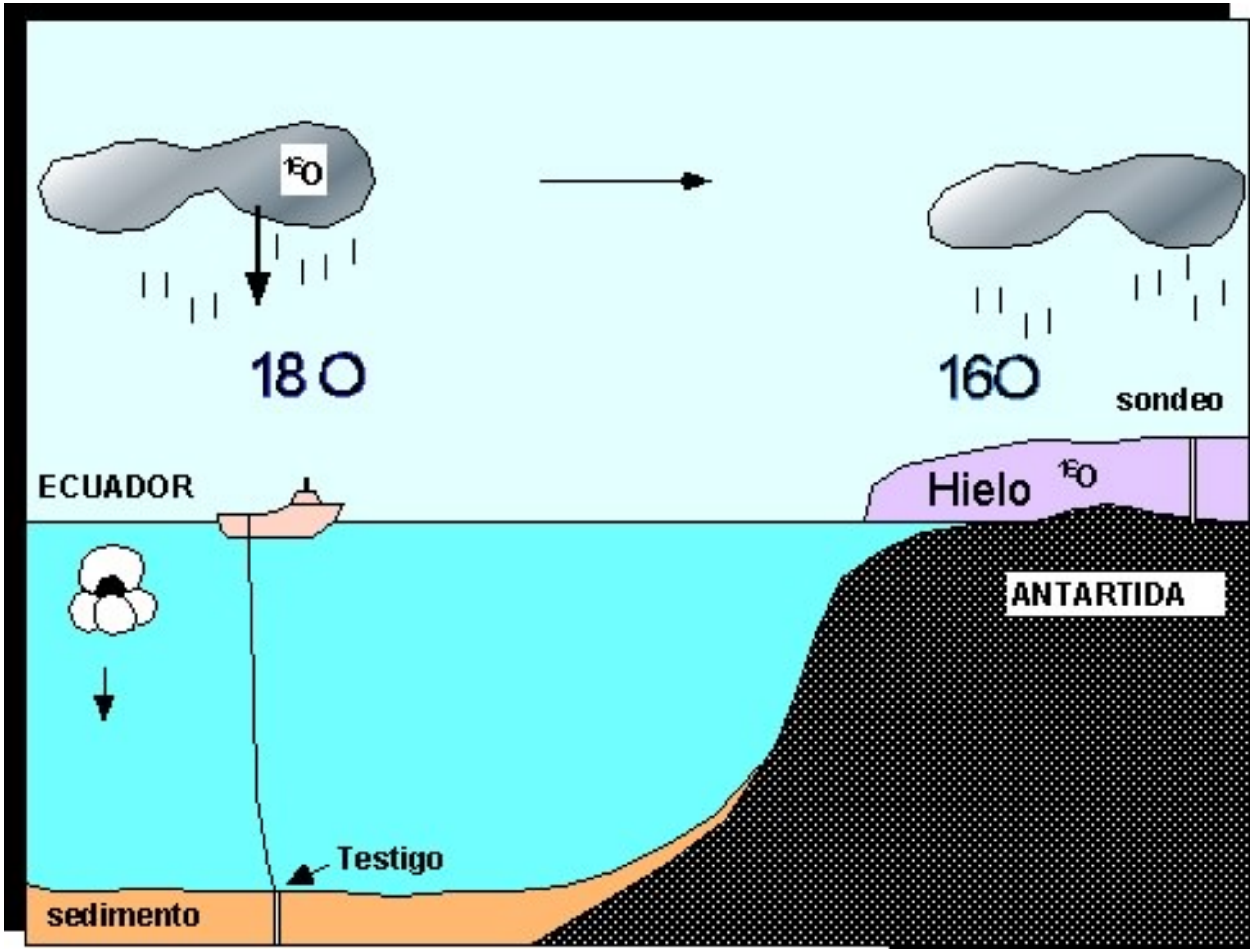




10 m of sea level change
4 million Km^3 of ice
0.l ‰ $\delta^{18}O$

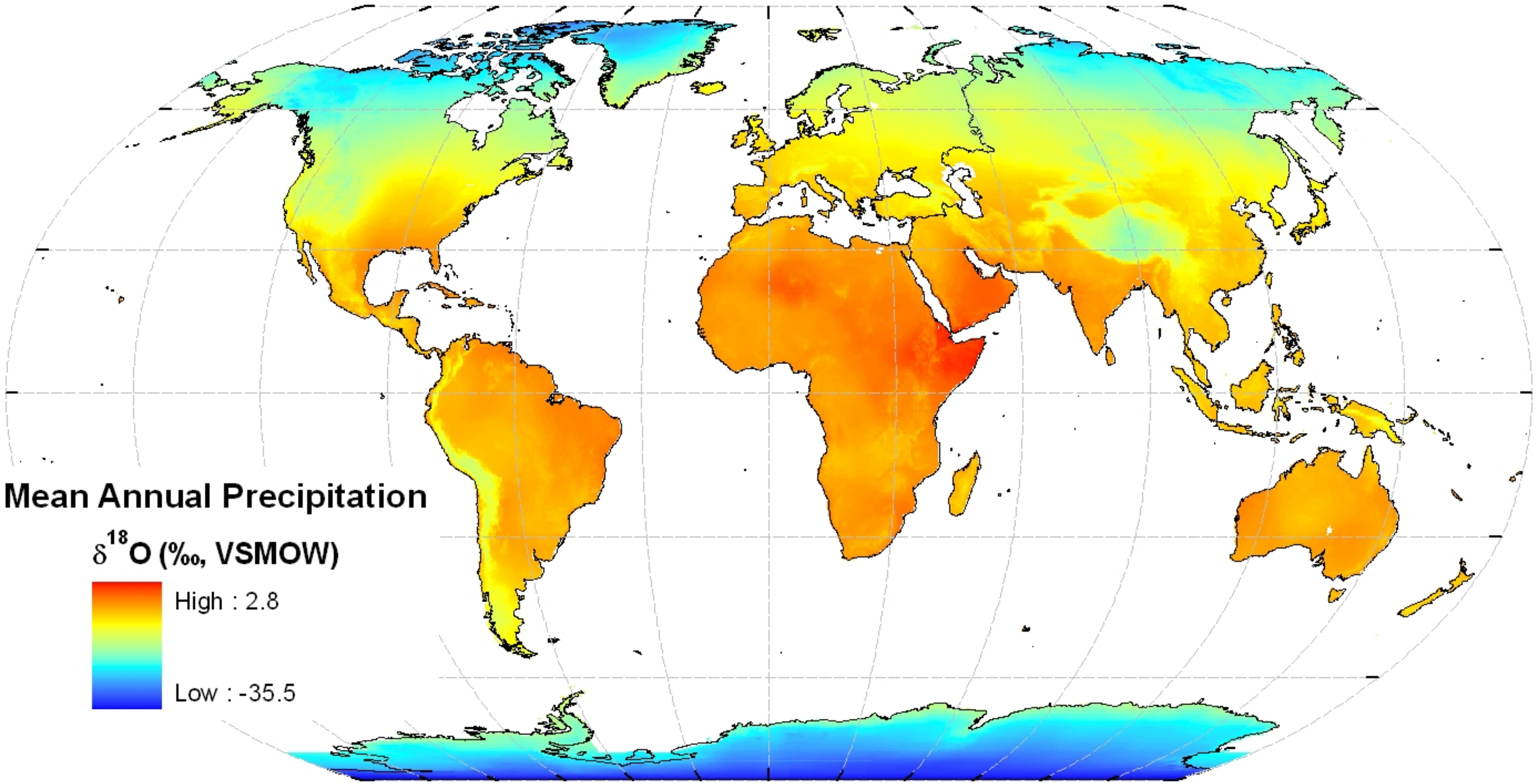
During the last glacial maximum, 20 ky ago, the Laurentide ice sheet in north America and the Fennoscandian ice sheet in NW Europe, together with the Antarctic and Greenland ice sheets store a huge amount of ice very enriched in ^{16}O. As a result a $\delta^{18}O$ global increase of 1 ‰ was recorded in foraminifers living at that time.

Why ice sheets are so enriched in ^{16}O

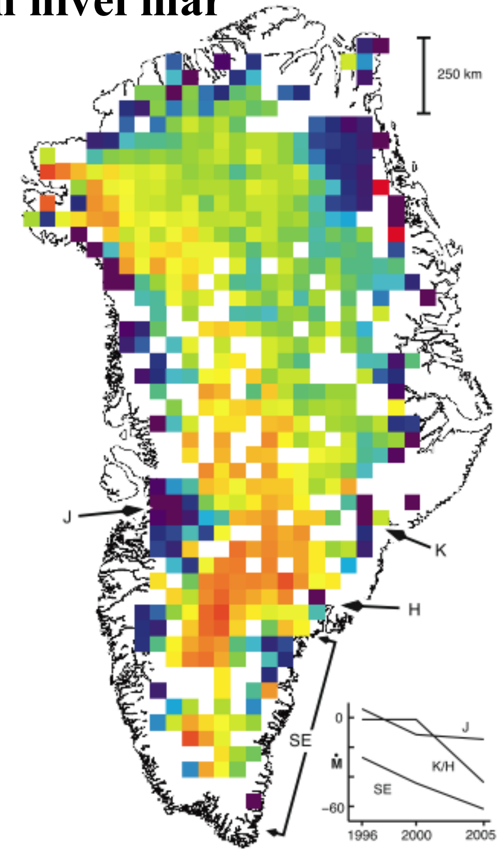


During condensation, the water droplets are enriched in ^{18}O, and the remaining vapor is enriched in ^{16}O.

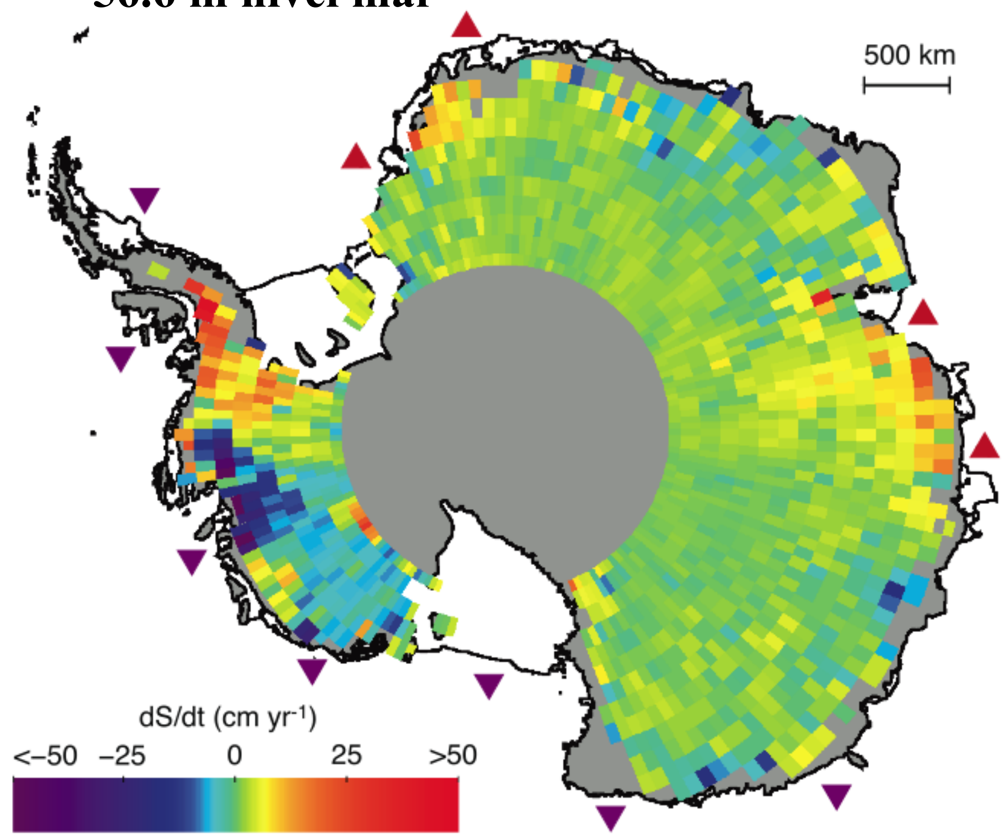
After a number of condensations water vapor that reaches the high latitudes is very enriched in ^{16}O

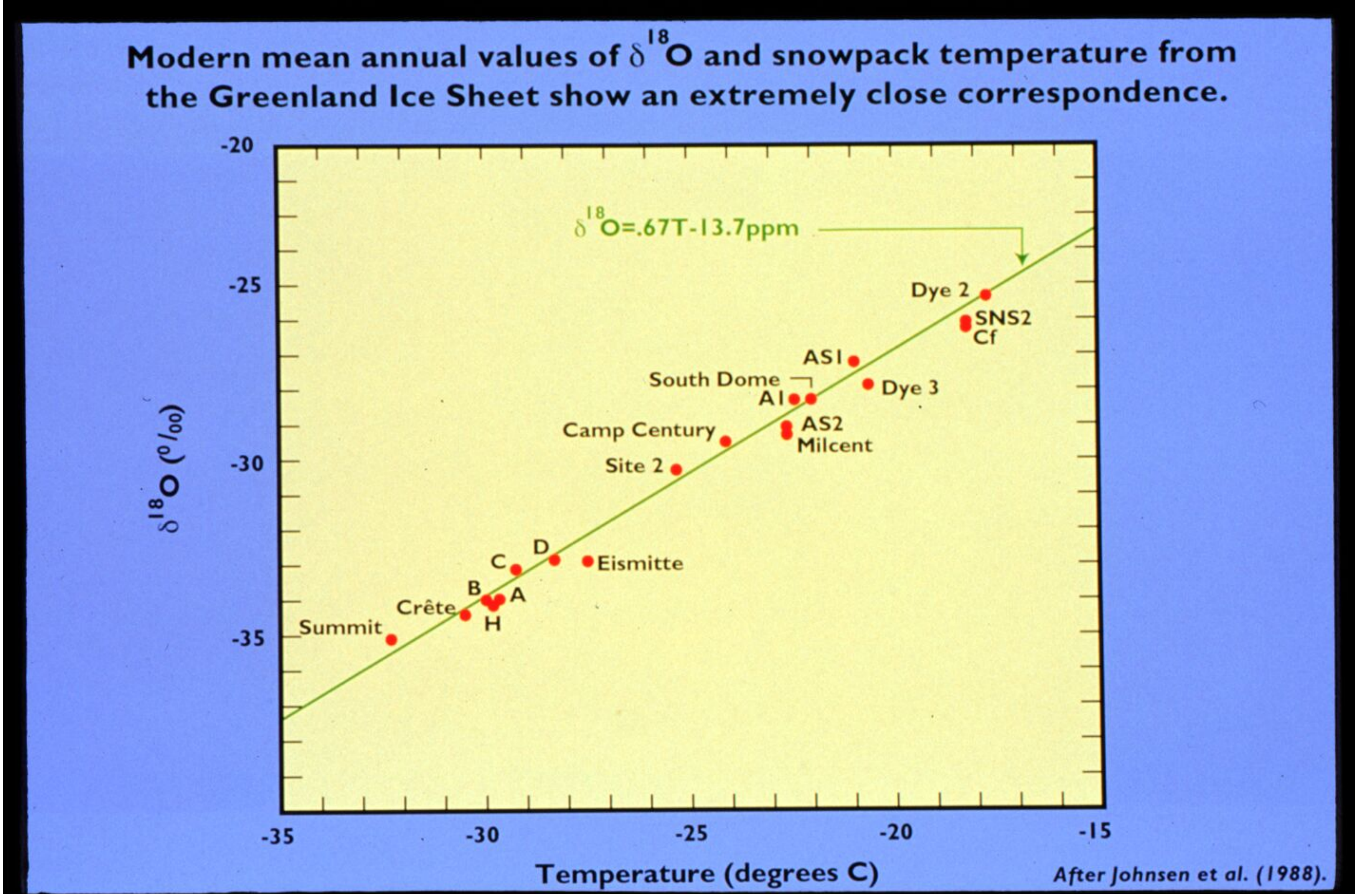

Mean Annual Precipitation
δ18O (‰, VSMOW)
High : 2.8
Low : -35.5

2,9 * 10^6 Km^3
7.3 m nivel mar



24,7 * 10^6 Km^3
56.6 m nivel mar





Cuanto mas frío está el aire y el vapor de agua mayor es la concentración de ^{16}O en el vapor de agua y por tanto en la nieve que precipita en Groenlandia. En el gráfico se ve que existe una excelente correlación entre la temperatura del aire y la relación $^{18}O/^{16}O$ isotópica de la nieve en distintos puntos de Groenlandia.

Influence of the local hydrologic cycle

Regional seawater $\delta^{18}O$:

Hydrologic budget = Precipitation+river runoff+ice calving-Evaporation
Relative contribution of the main freshwater sources

$\delta^{18}O$ of the different freshwater sources

$\delta^{18}O$ of rainfall+ $\delta^{18}O$ runoff + $\delta^{18}O$ ice - $\delta^{18}O$ of evaporated water

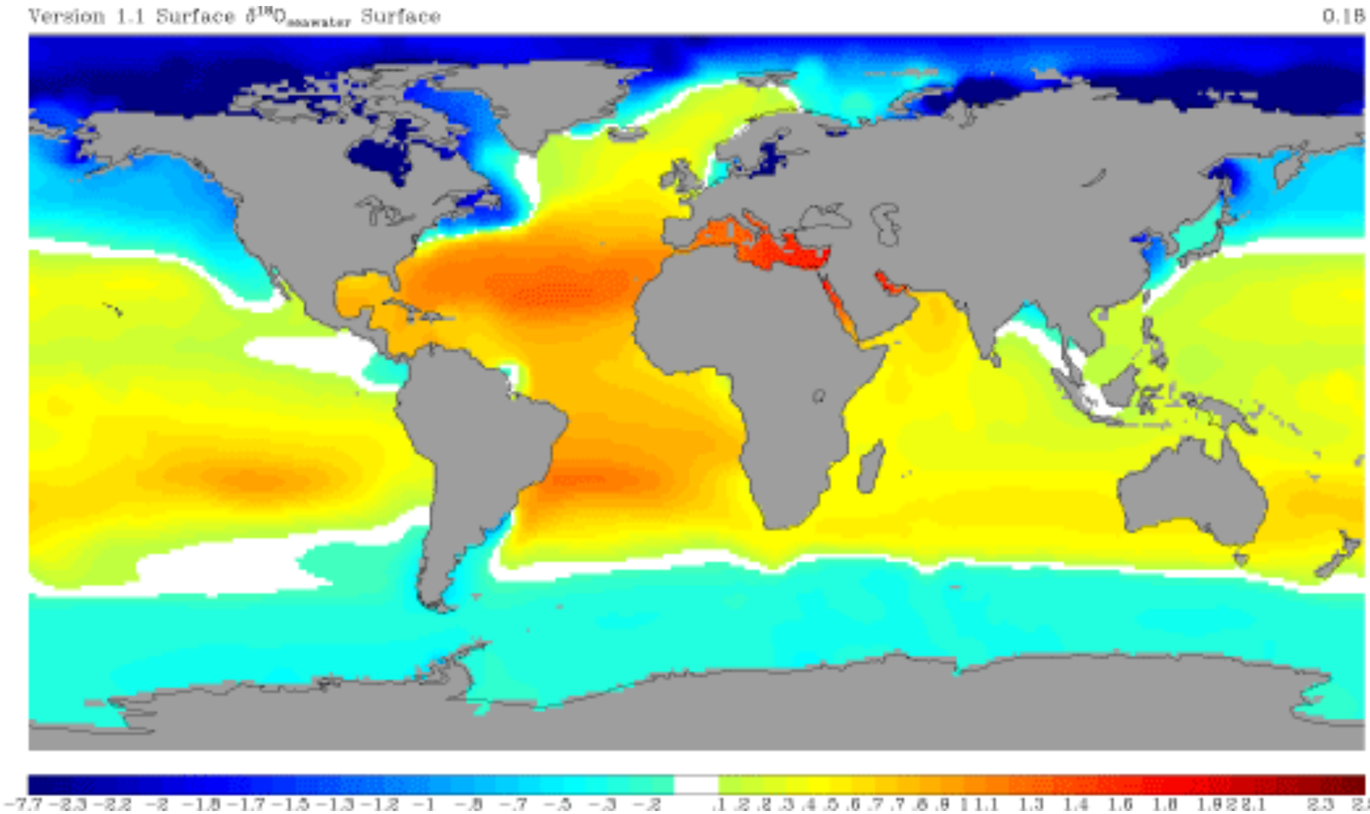
During evaporation, seawater is enriched in ^{18}O

Rainfall and runoff are usually enriched in ^{16}O depending on the freshwater source.
Ice is always highly enriched in ^{16}O

D18O of the Mediterranean main freshwater sources

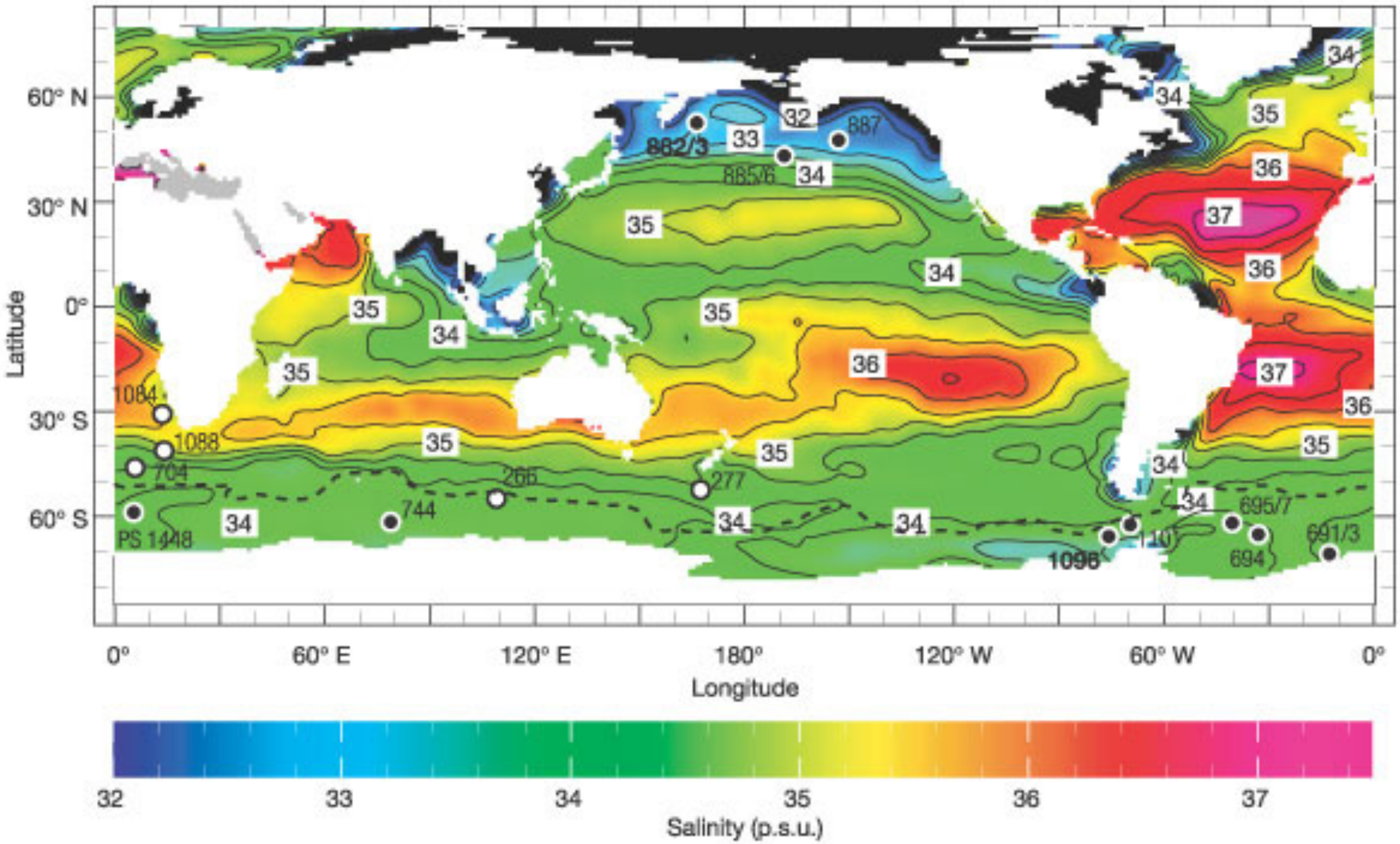
Nile water +2‰ **to** +4‰
Rhone water -13‰ to -14‰
Danube water (Black Sea) -10.3‰ **to** -13.3‰

Surface seawater $\delta^{18}O$



The hydrologic budget in the Ocean drives both salinity and seawater $\delta^{18}O$. In regions where evaporation is higher than precipitation the seawater $\delta^{18}O$ is higher, while in regions where precipitation is higher the $\delta^{18}O$ is more negative.

Global map of sea surface salinity



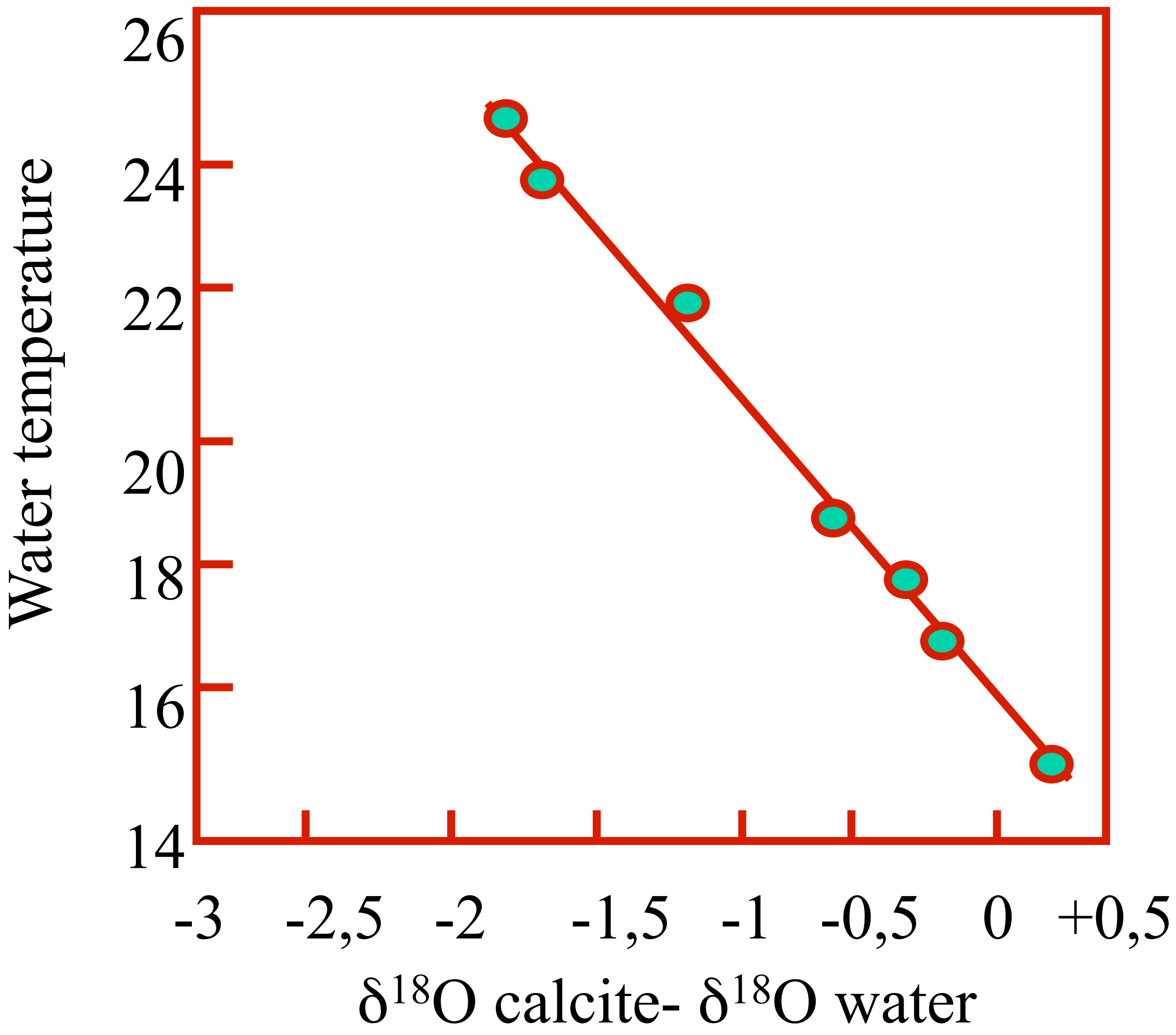
Influence of the seawater temperature during calcification on the $\delta^{18}O$ of foraminifers

$$Ca^{2+} + 2HCO^{3-} \Leftrightarrow CaCO_3 + CO_2 + H_2O$$

The equilibrium fractionation factor between calcite and water is a function of temperature

0.23 ‰ decrease in carbonate $\delta^{18}O$ relative to seawater $\delta^{18}O$ for every 1ºC temperature increase

Relation of foraminifer d18O and calcification temperature



Empirical method growing foraminifers in the lab.

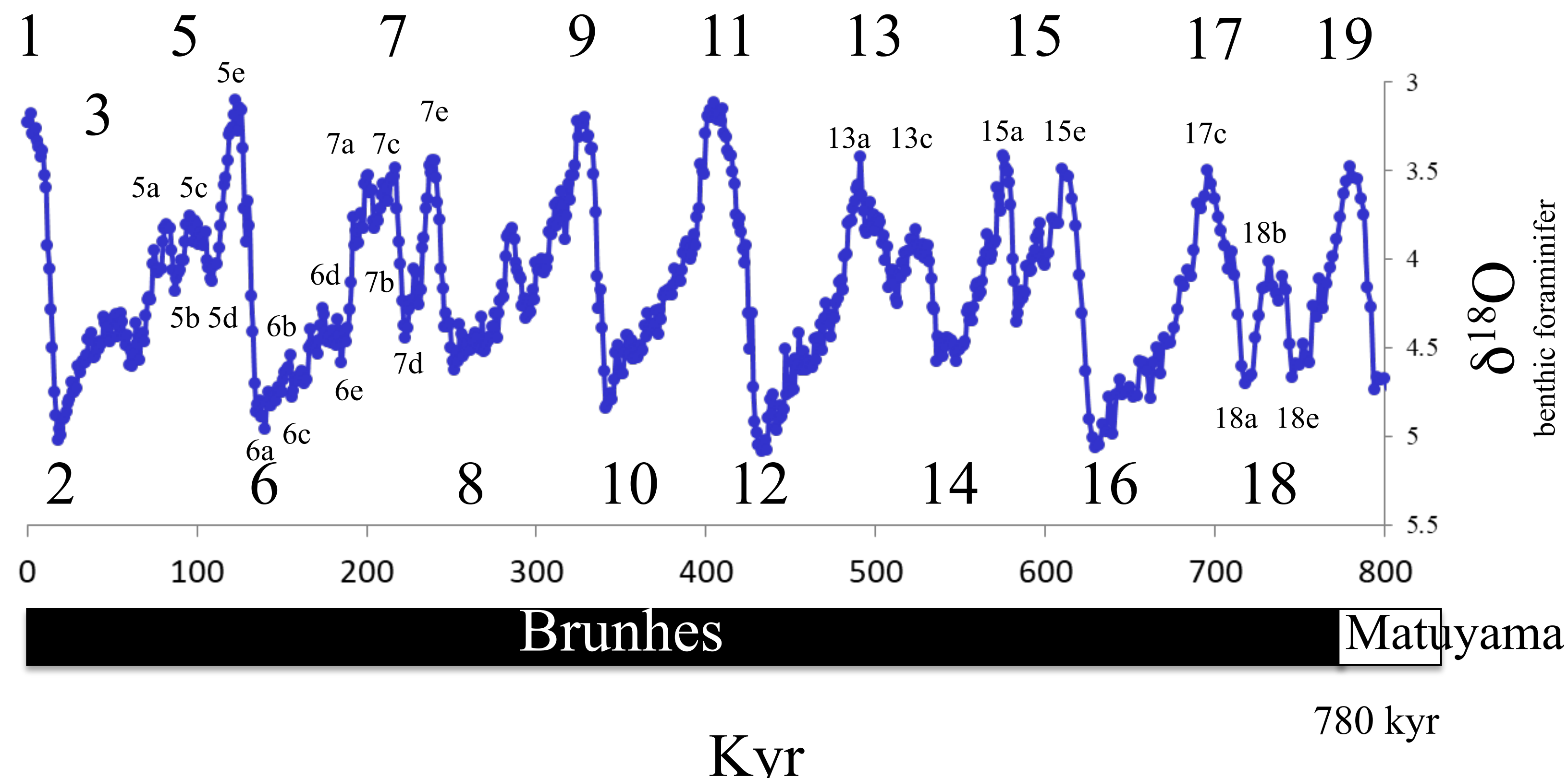
Growth of foraminifers in seawater with constant $\delta^{18}O$ at different temperatures.
as the temperature increases the $\delta^{18}O$ of the shell is lighter than the water $\delta^{18}O$

Bemis et al. 1998

Global LR04 benthic oxygen isotope Stack Lisiecki & Raymo 2005

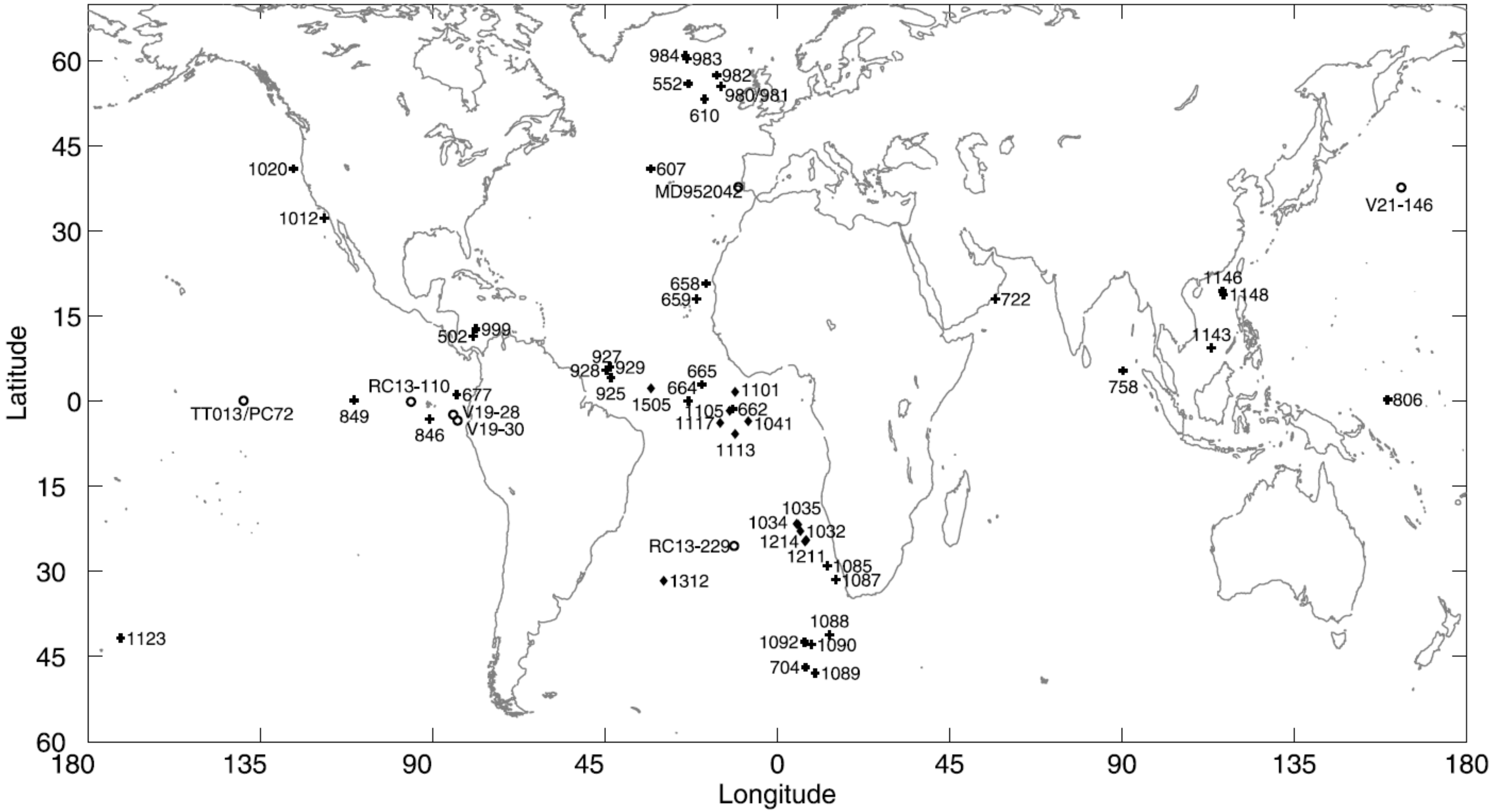
Isotope Time Scale

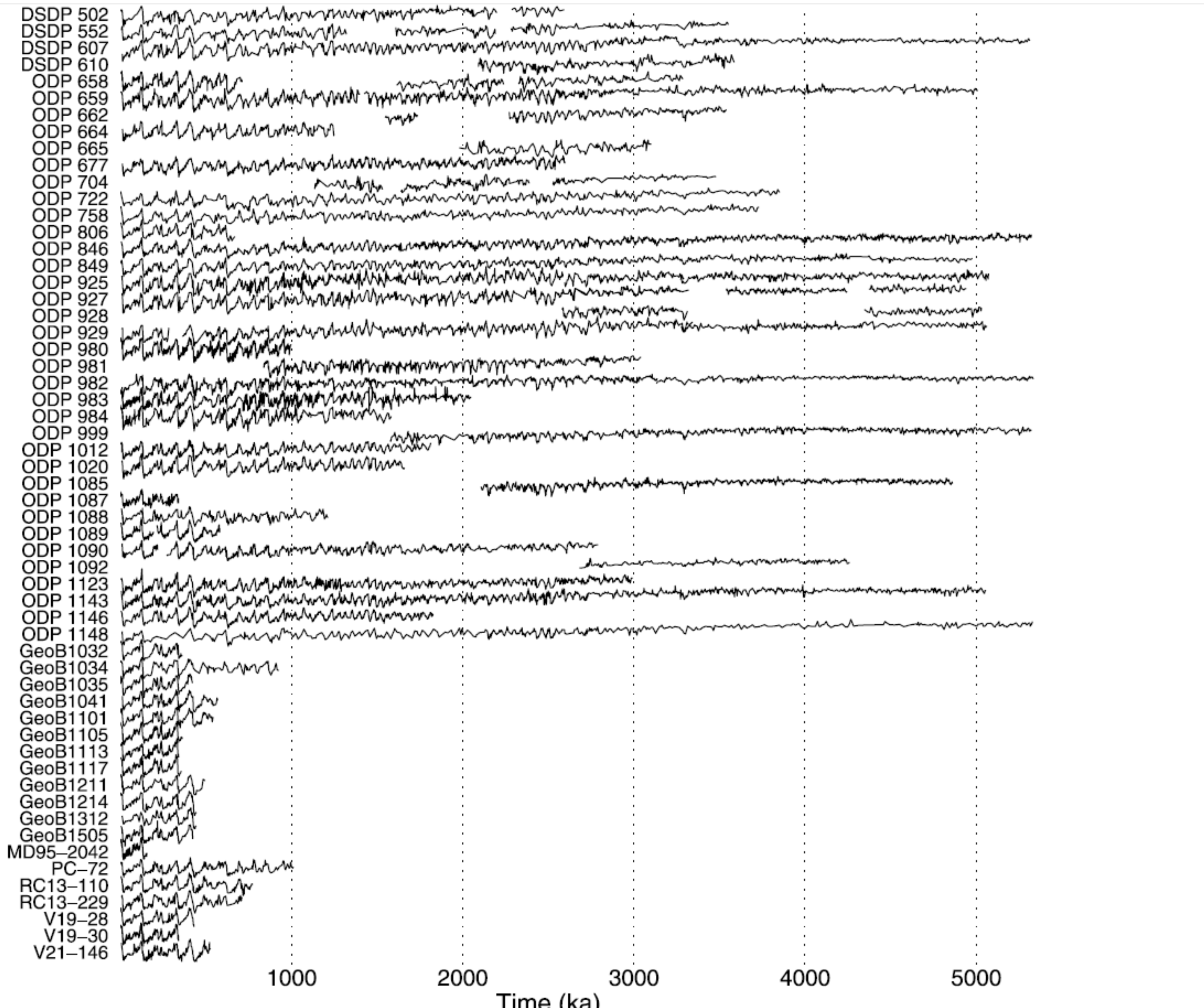
Marine Isotope Stages (MIS)

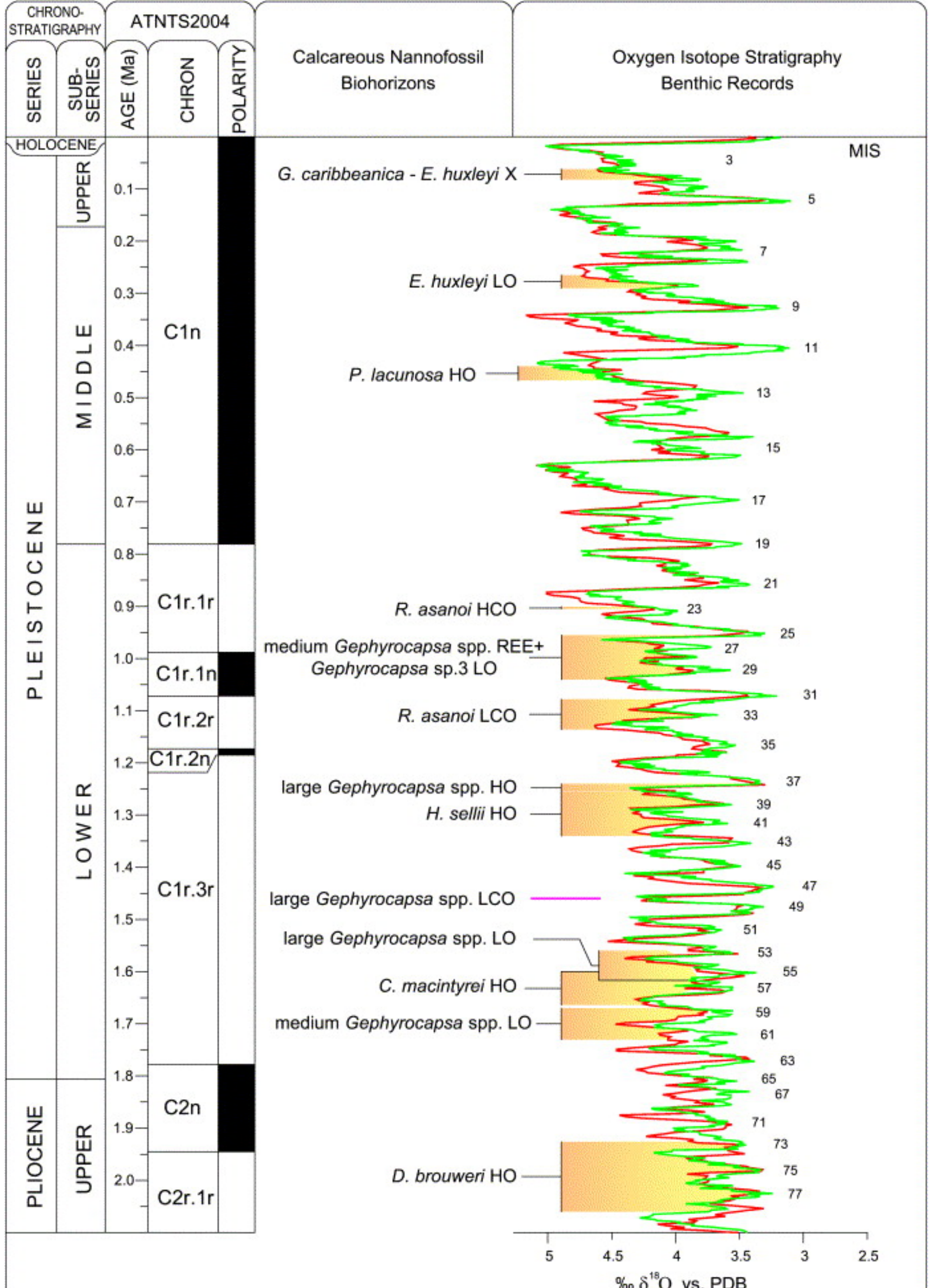


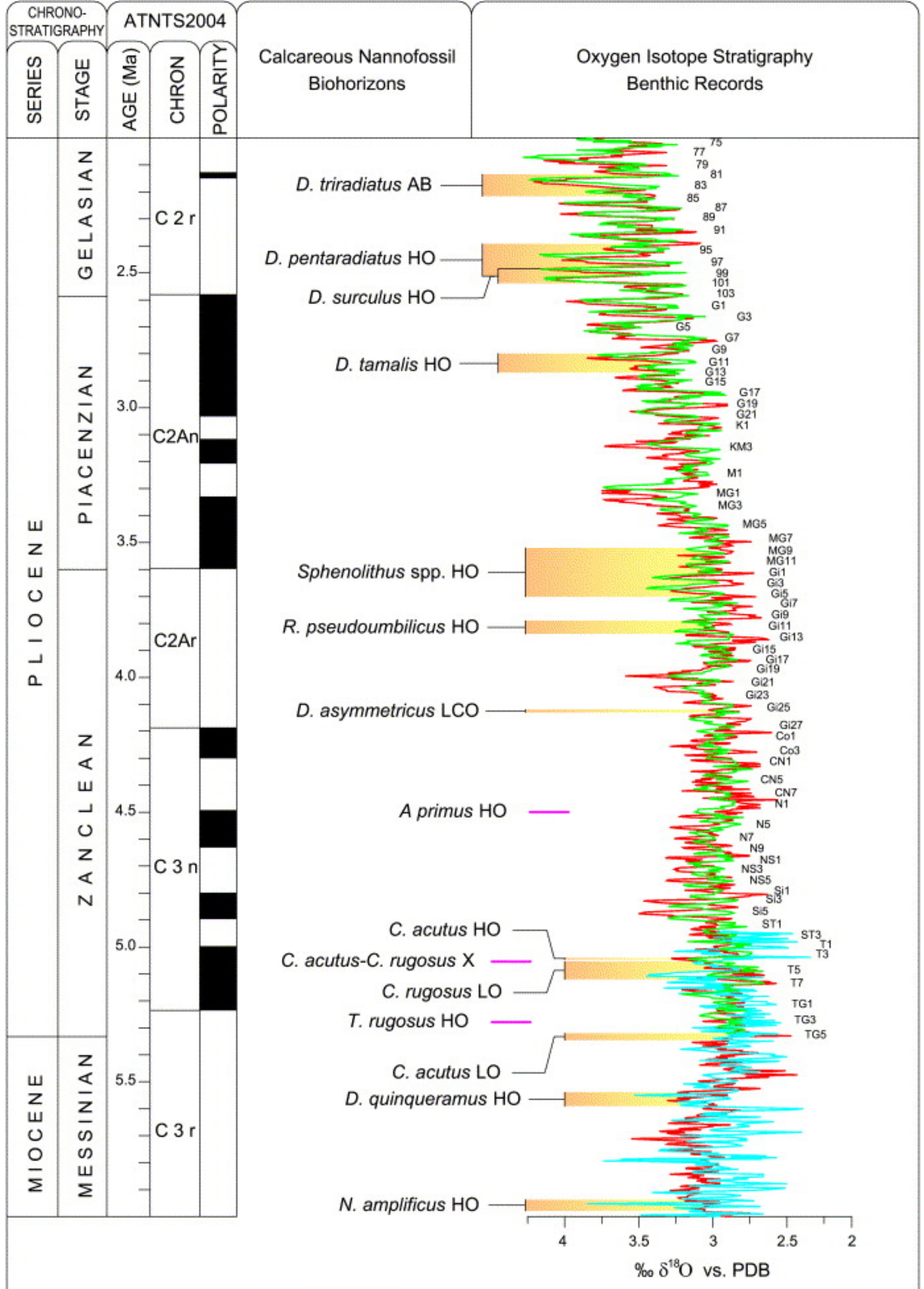
Benthic d18O records from 57 globally distributed sites

PA1003 LISIECKI AND RAYMO: PLIOCENE-PLEISTOCENE BENTHIC STACK **PA1003**

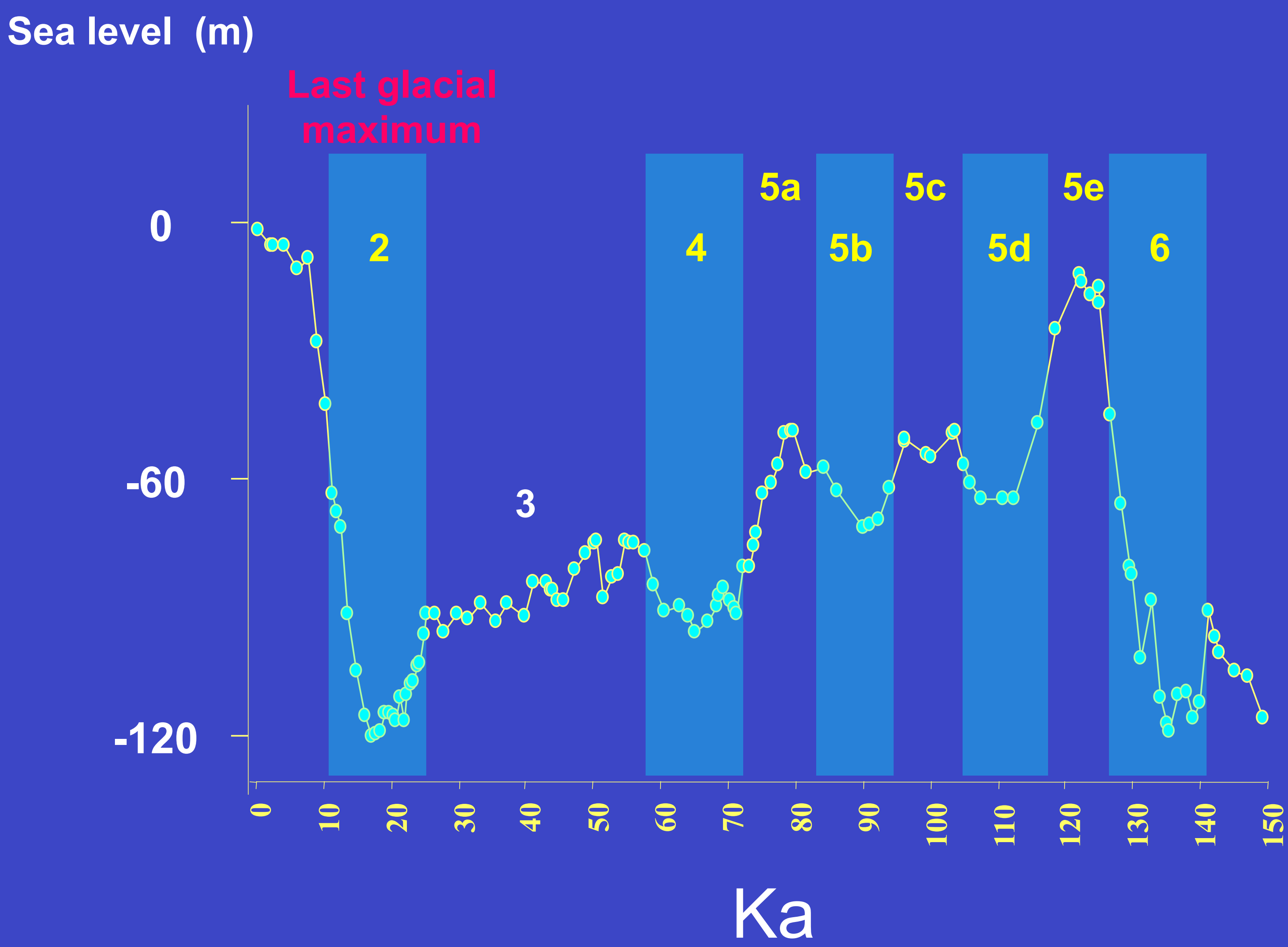


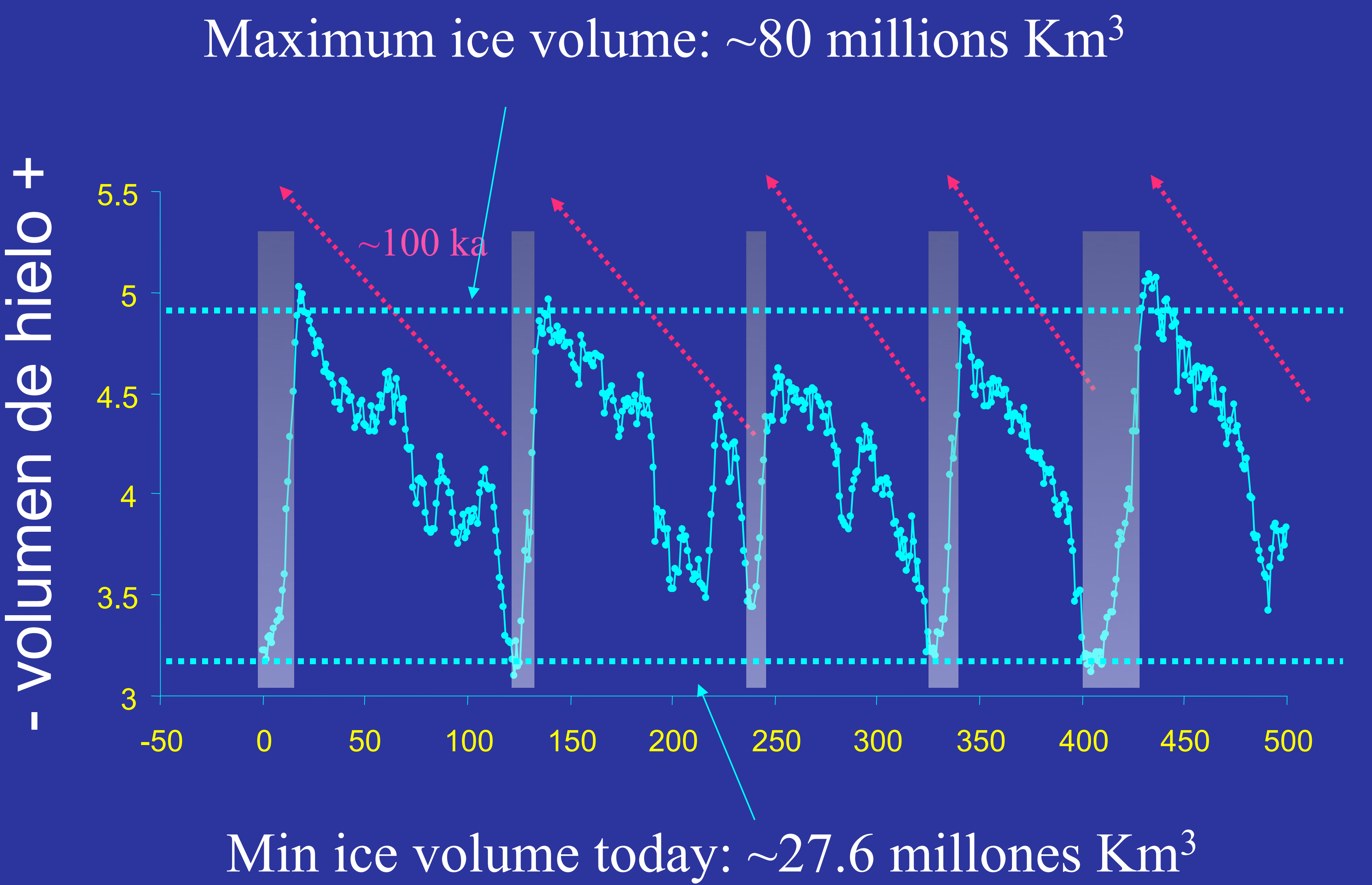

DSDP 502
DSDP 552
DSDP 607
DSDP 610
ODP 658
ODP 659
ODP 662
ODP 664
ODP 665
ODP 677
ODP 704
ODP 722
ODP 758
ODP 806
ODP 846
ODP 849
ODP 925
ODP 927
ODP 928
ODP 929
ODP 980
ODP 981
ODP 982
ODP 983
ODP 984
ODP 999
ODP 1012
ODP 1020
ODP 1085
ODP 1087
ODP 1088
ODP 1089
ODP 1090
ODP 1092
ODP 1123
ODP 1143
ODP 1146
ODP 1148
GeoB1032
GeoB1034
GeoB1035
GeoB1041
GeoB1101
GeoB1105
GeoB1113
GeoB1117
GeoB1211
GeoB1214
GeoB1312
GeoB1505
MD95–2042
PC–72
RC13–110
RC13–229
V19–28
V19–30
V21–146
1000
2000
3000
4000
5000
Time (ka)


CHRONO-STRATIGRAPHY
ATNTS2004
SERIES
SUB-SERIES
AGE (Ma)
CHRON
POLARITY
Calcareous Nannofossil Biohorizons
Oxygen Isotope Stratigraphy Benthic Records
HOLOCENE
PLEISTOCENE
PLIOCENE
UPPER
MIDDLE
LOWER
UPPER
C1n
C1r.1r
C1r.1n
C1r.2r
C1r.2n
C1r.3r
C2n
C2r.1r
MIS
G. caribbeanica - E. huxleyi X
E. huxleyi LO
P. lacunosa HO
R. asanoi HCO
medium Gephyrocapsa spp. REE+
Gephyrocapsa sp.3 LO
R. asanoi LCO
large Gephyrocapsa spp. HO
H. sellii HO
large Gephyrocapsa spp. LCO
large Gephyrocapsa spp. LO
C. macintyrei HO
medium Gephyrocapsa spp. LO
D. brouweri HO
‰ δ18O vs. PDB

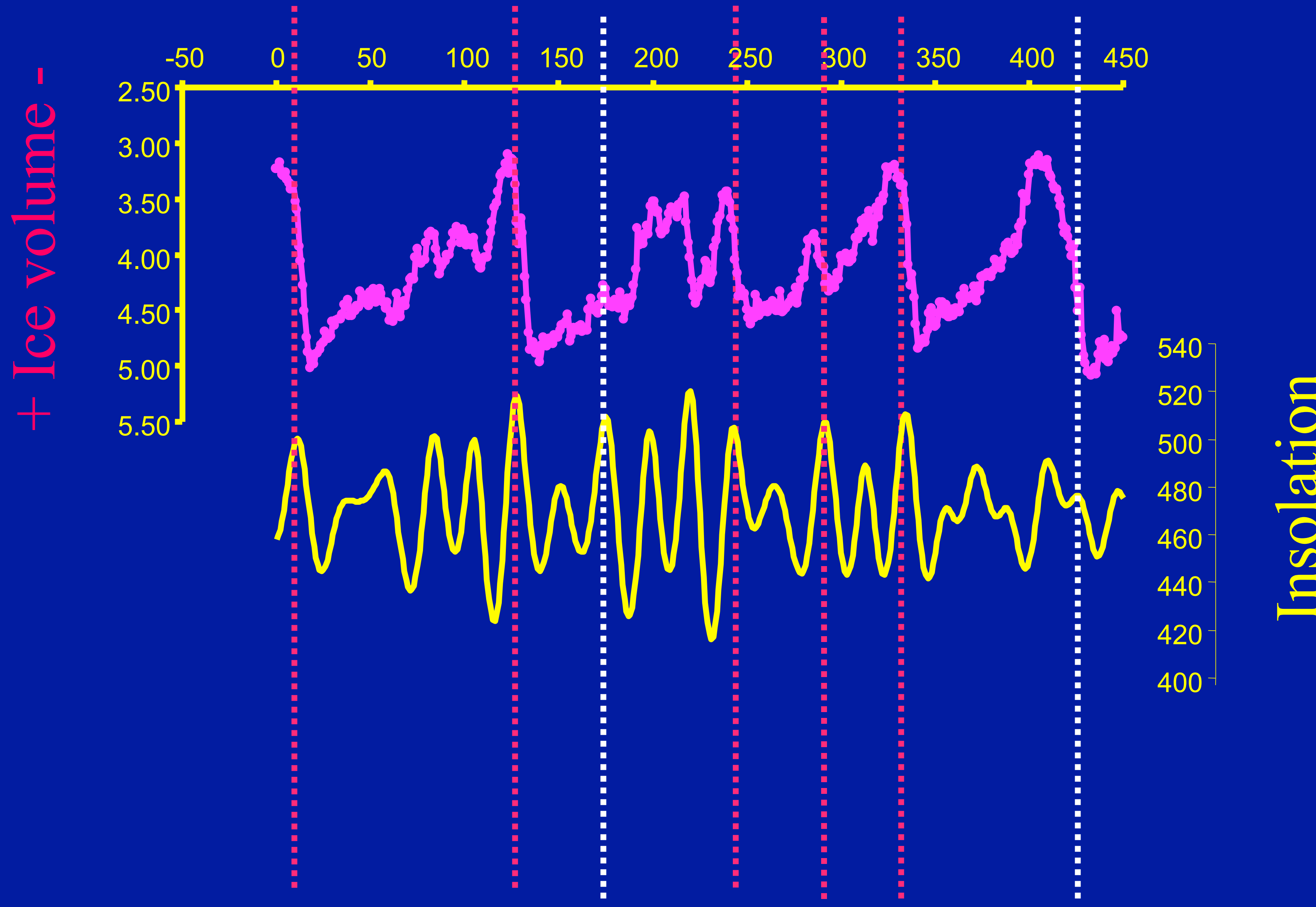


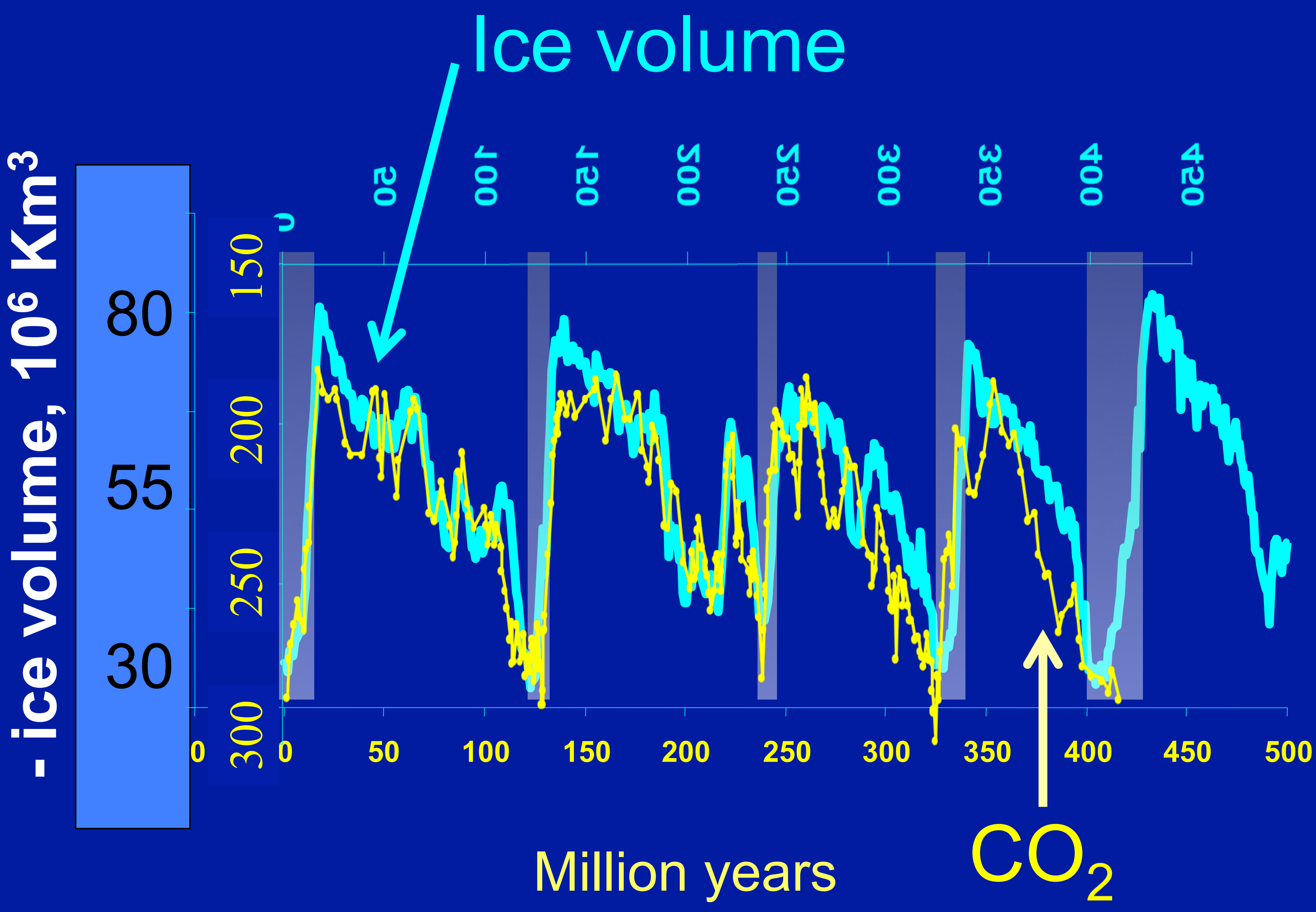
CHRONO-STRATIGRAPHY
ATNTS2004
SERIES
STAGE
AGE (Ma)
CHRON
POLARITY
Calcareous Nannofossil Biohorizons
Oxygen Isotope Stratigraphy Benthic Records
PLIOCENE
MIOCENE
GELASIAN
PIACENZIAN
ZANCLEAN
MESSINIAN
2.5
3.0
3.5
4.0
4.5
5.0
5.5
C 2 r
C2An
C2Ar
C 3 n
C 3 r
D. triradiatus AB
D. pentaradiatus HO
D. surculus HO
D. tamalis HO
Sphenolithus spp. HO
R. pseudoumbilicus HO
D. asymmetricus LCO
A primus HO
C. acutus HO
C. acutus-C. rugosus X
C. rugosus LO
T. rugosus HO
C. acutus LO
D. quinqueramus HO
N. amplificus HO
75
77
79
81
83
85
87
89
91
95
97
99
101
103
G1
G3
G5
G7
G9
G11
G13
G15
G17
G19
G21
K1
KM3
M1
MG1
MG3
MG5
MG7
MG9
MG11
Gi1
Gi3
Gi5
Gi7
Gi9
Gi11
Gi13
Gi15
Gi17
Gi19
Gi21
Gi23
Gi25
Gi27
Co1
Co3
CN1
CN5
CN7
N1
N5
N7
N9
NS1
NS3
NS5
Si1
Si3
Si5
ST1
ST3
T1
T3
T5
T7
TG1
TG3
TG5
4
3.5
3
2.5
2
‰ δ18O vs. PDB


Sea level (m)
Last glacial maximum
0
-60
-120
2
3
4
5a
5b
5c
5d
5e
6
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
Ka



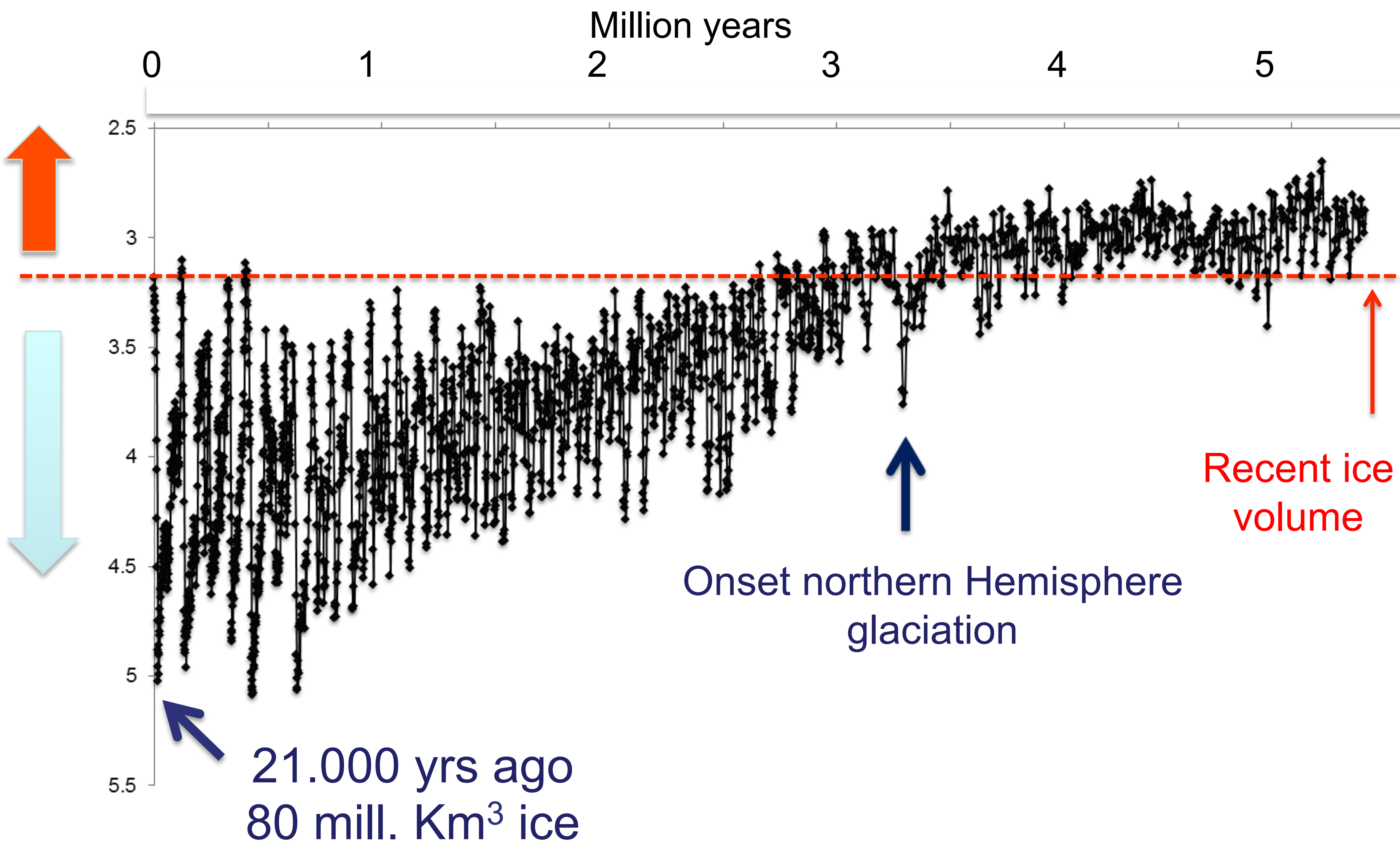
Maximum ice volume: ~80 millions Km3
- volumen de hielo +
~100 ka
5.5
5
4.5
4
3.5
3
-50
0
50
100
150
200
250
300
350
400
450
500
Min ice volume today: ~27.6 millones Km3

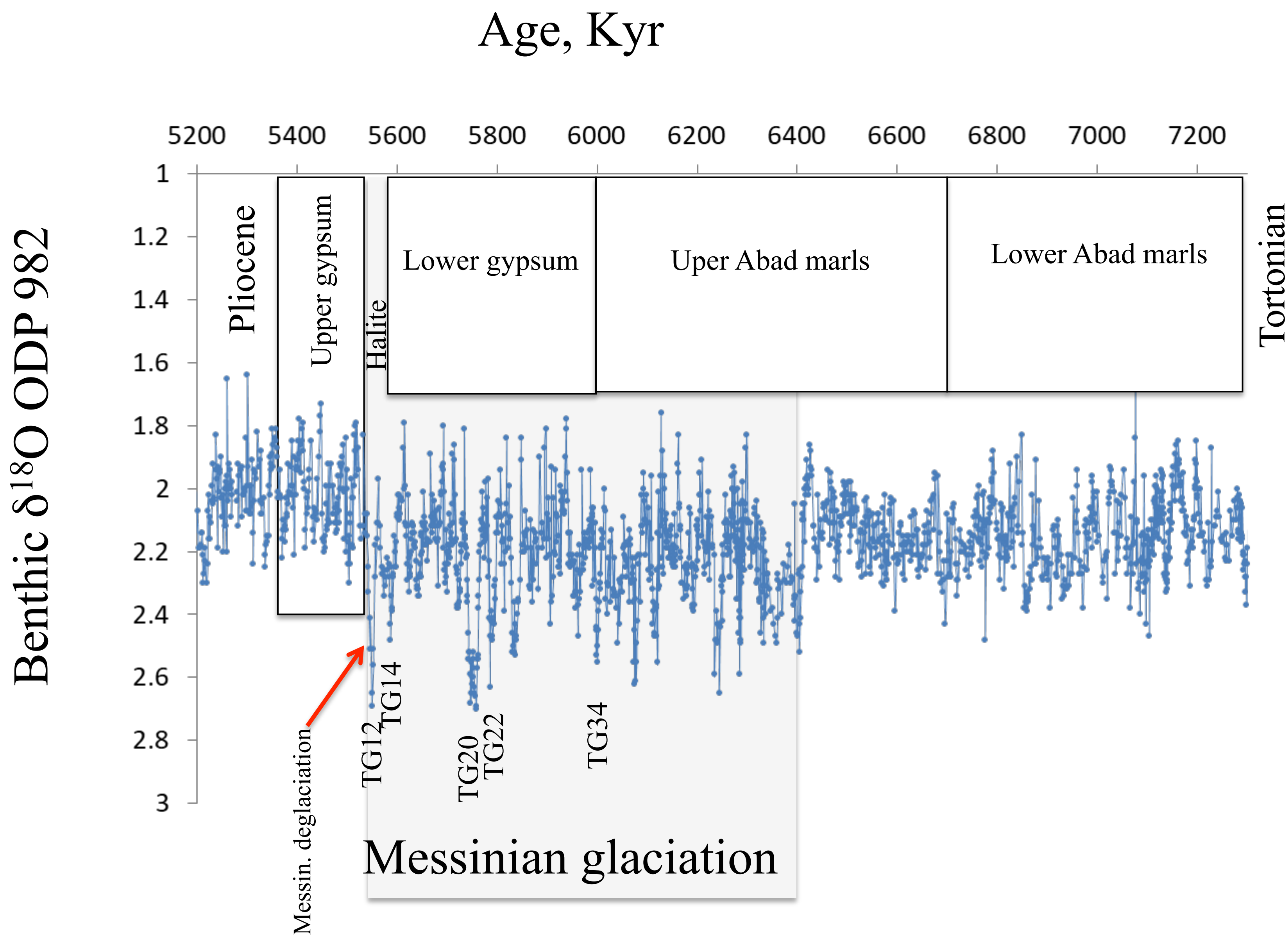

+ Ice volume -
-50
0
50
100
150
200
250
300
350
400
450
2.50
3.00
3.50
4.00
4.50
5.00
5.50
540
520
500
480
460
440
420
400
Insolation



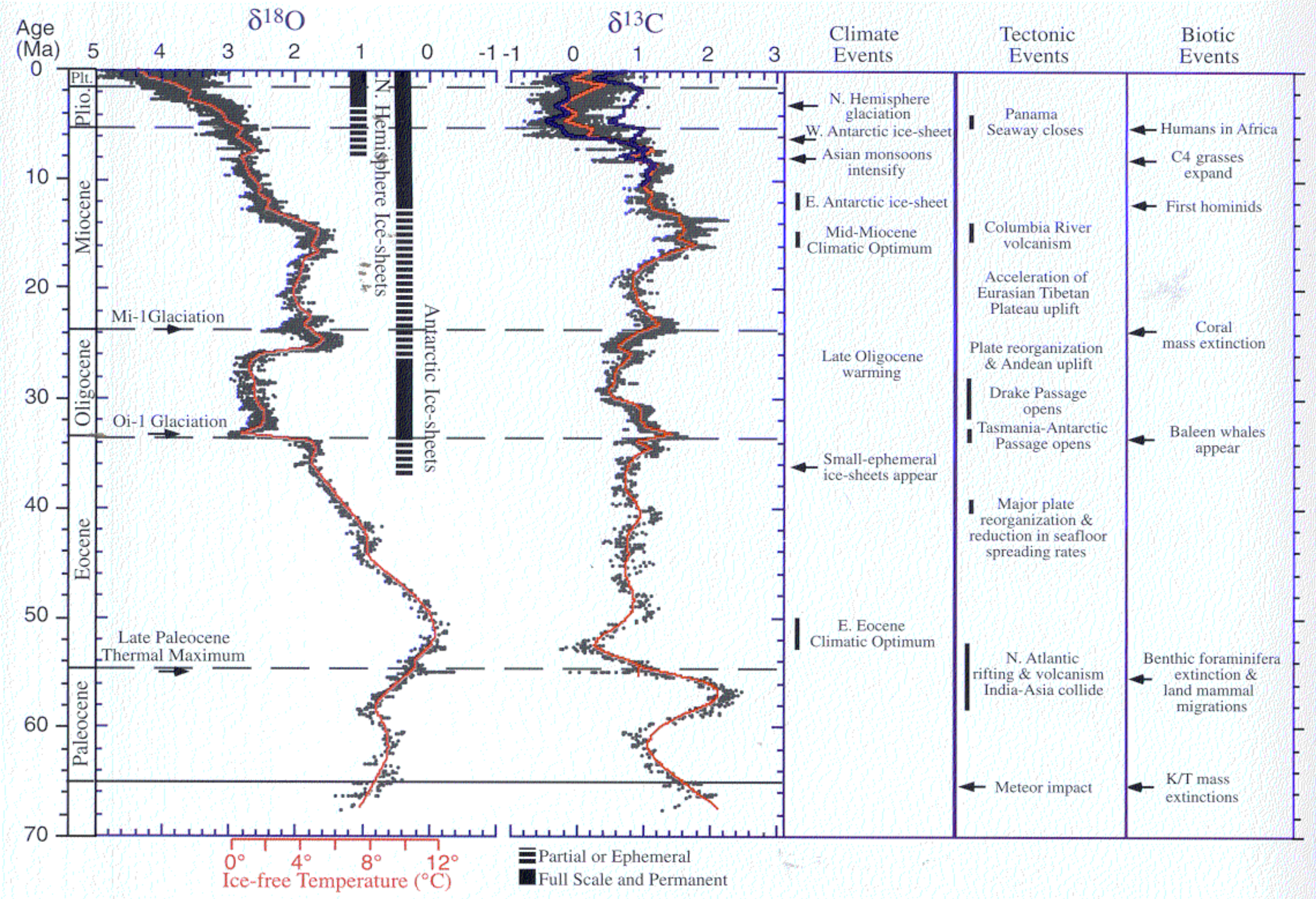
Ice volume
- ice volume, 10^6 Km^3
80
55
30
150
200
250
300
0
50
100
150
200
250
300
350
400
450
500
Million years
CO_2

LR04 $\delta^{18}O$ stack Lisiecki and Raymo 2005



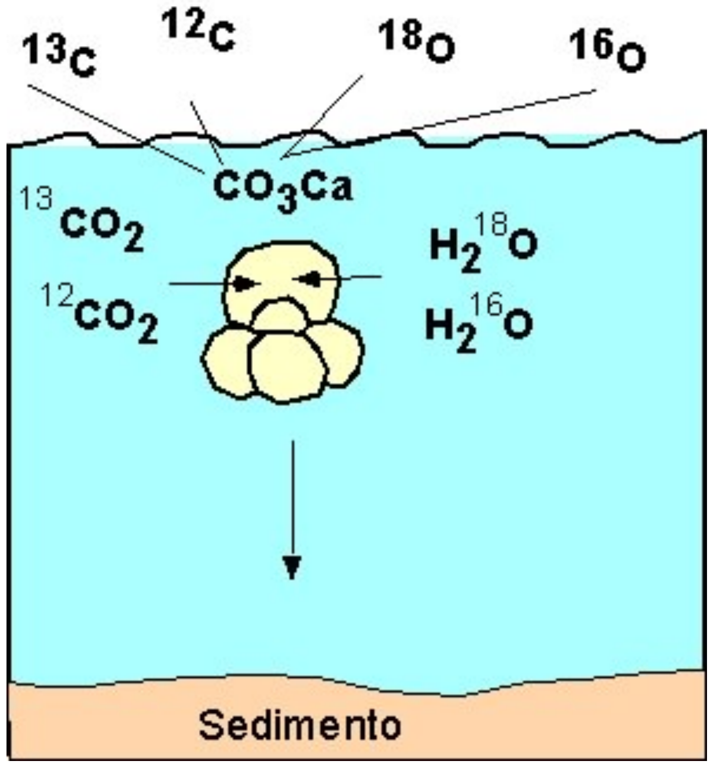


Age, Kyr
5200
5400
5600
5800
6000
6200
6400
6600
6800
7000
7200
Benthic δ18O ODP 982
1
1.2
1.4
1.6
1.8
2
2.2
2.4
2.6
2.8
3
Pliocene
Upper gypsum
Halite
Lower gypsum
Uper Abad marls
Lower Abad marls
Tortonian
Messin. deglaciation
TG12
TG14
TG20
TG22
TG34
Messinian glaciation



d18O record from the K/T boundary to the Holocene. During the Cretaceous Paleocene and Eocene there was no ice on Earth. The Greenhouse Earth. Near the Eocene-Oligocene boundary, ice started to accumulate in Antarctica. This was the onset of the Icehouse Earth. In the Mid Pliocene ice sheets also expanded in the northern Hemisphere.

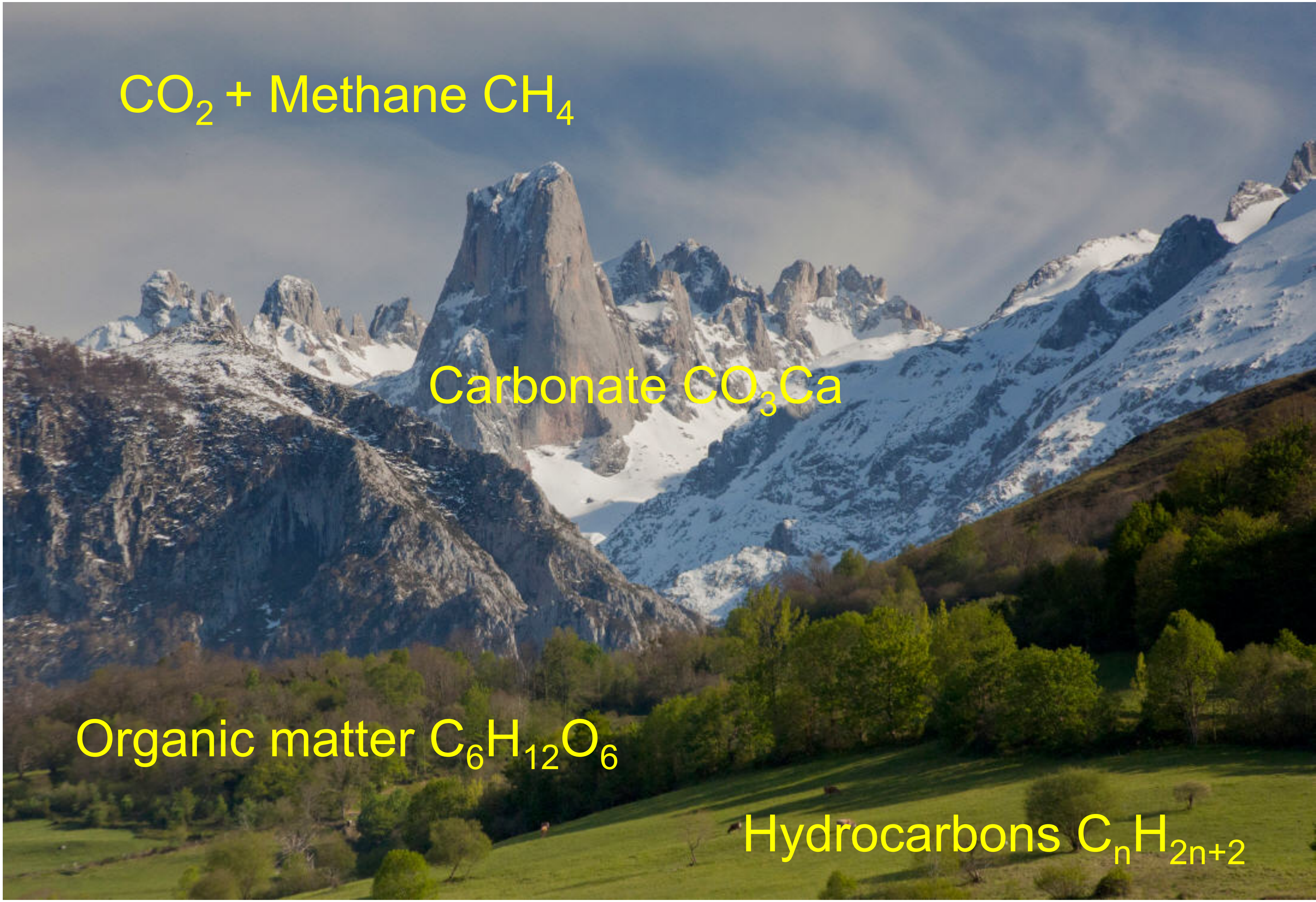
Stable carbon isotopes in Foraminifers

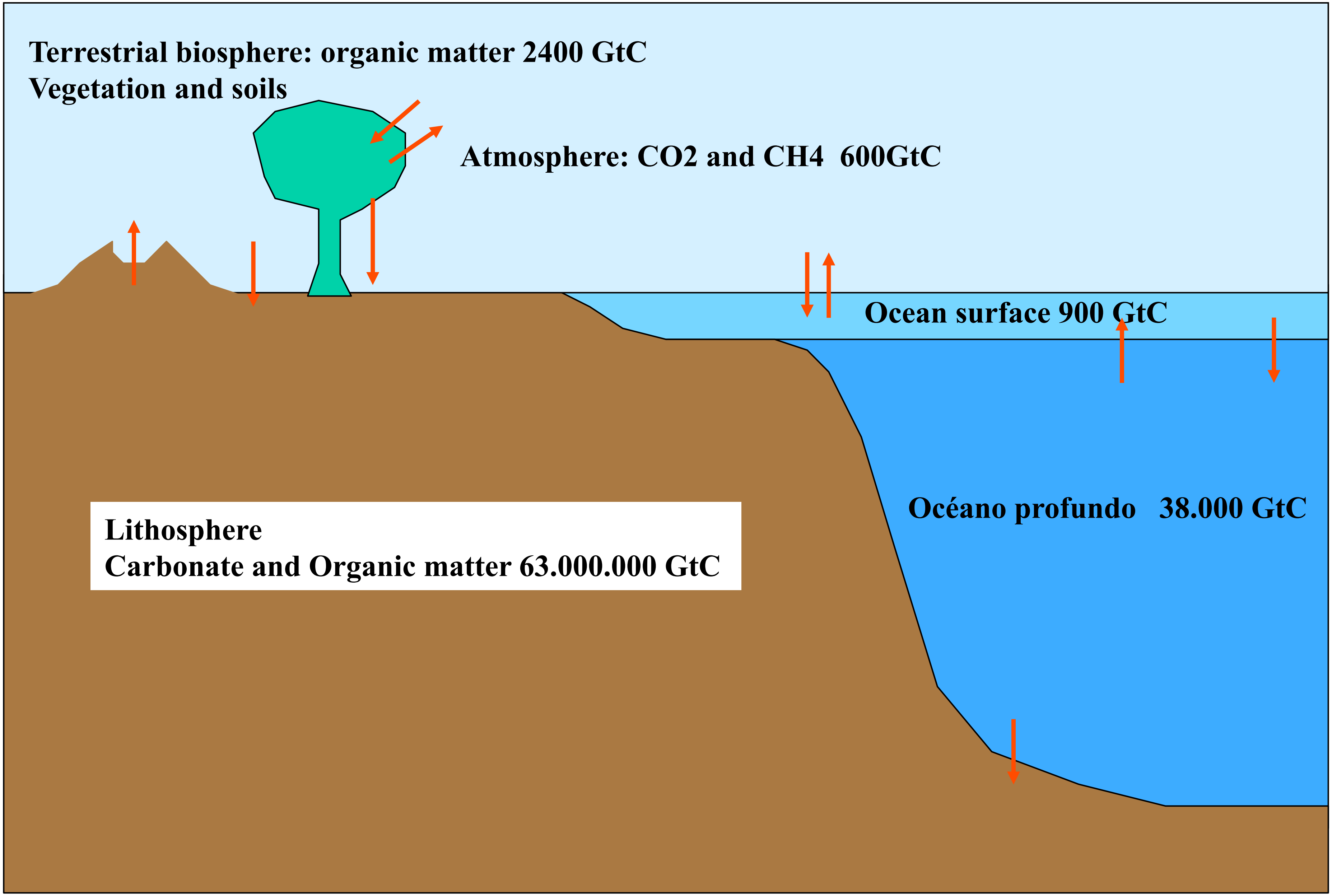


^{12}C 98.89 %
^{13}C 1.11%

The $\delta^{13}C$ of foraminifer shells is controlled by the $\delta^{13}C_{DIC}$ in seawater, mainly by $\delta^{13}C$ of HCO_3^-

Commonly, foraminifer carbonate deviates from carbonate precipitated in isotope equilibrium with seawater due to vital effects, associated to the incorporation of metabolic CO_2
In recent species deviations from equilibrium are known.


CO_2 + Methane CH_4
Carbonate CO_3Ca
Organic matter $C_6H_{12}O_6$
Hydrocarbons C_nH_{2n+2}


Terrestrial biosphere: organic matter 2400 GtC
Vegetation and soils
Atmosphere: CO2 and CH4 600GtC
Ocean surface 900 GtC
Océano profundo   38.000 GtC
Lithosphere
Carbonate and Organic matter 63.000.000 GtC

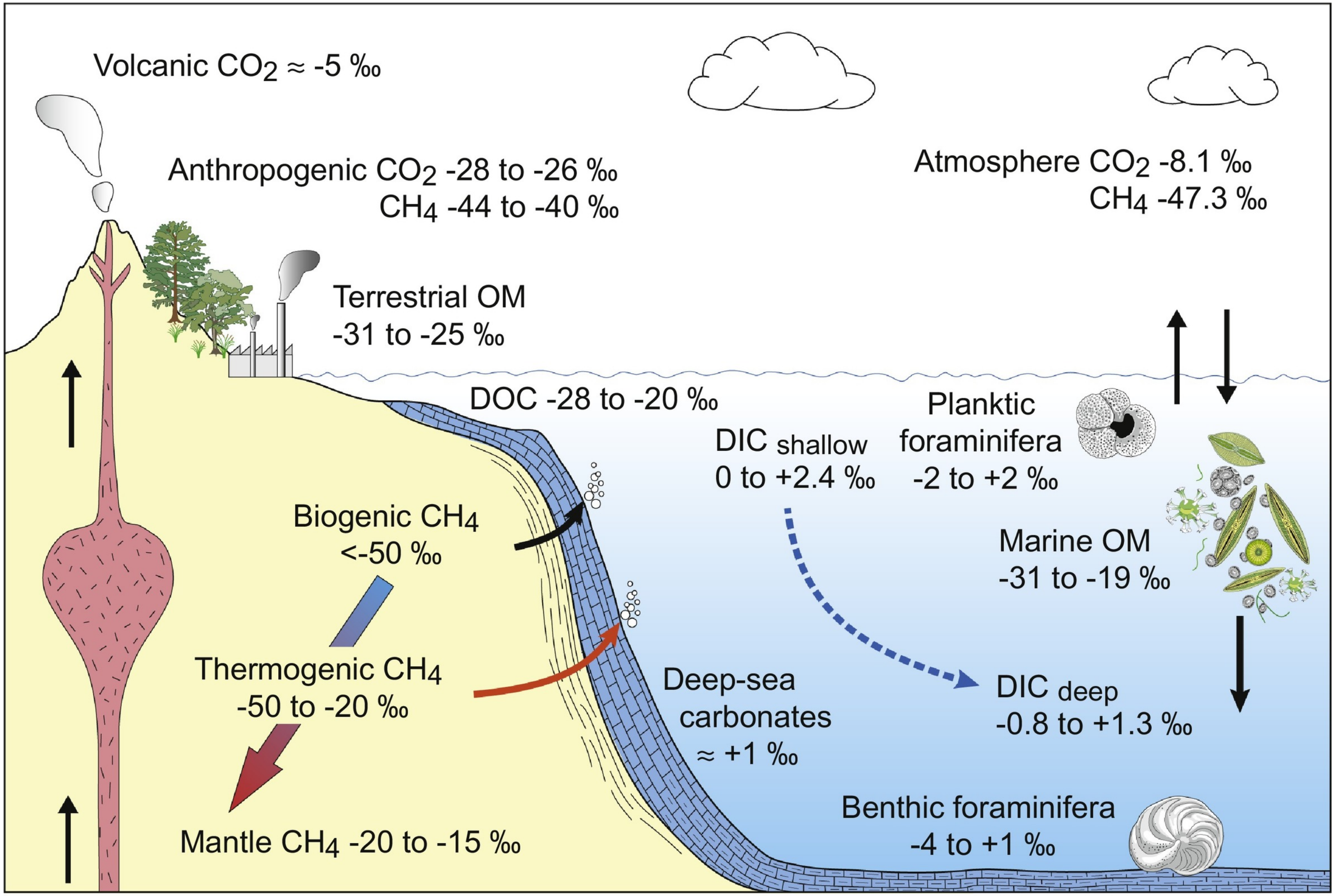
Main carbon reservoirs on Earth		Average $\delta^{13}C$
Ocean:	DIC	0 - +2‰
Biosphere:		-20 -30 ‰
Atmosphere:		-7 ‰
Lithosphere:	Carbonate…..	1 ‰
	Hydrocarbons	-20-40 ‰

$$6CO_2 + 6H_2O + N \underset{\text{Respiration Oxidation}}{\overset{\text{Photosynthesis}}{\rightleftarrows}} C_6H_{12}O_6 + 6O_2$$

During conversion of inorganic carbon into organic carbon plants and phytoplankton have a strong preference for ^{12}C. Plants remove ^{12}C from the atmosphere and phytoplankton from the surface Ocean.

Organic carbon is usually depleted in ^{13}C

The $\delta^{13}C$ of the different species of the carbonate system is regulated by the carbon cycle

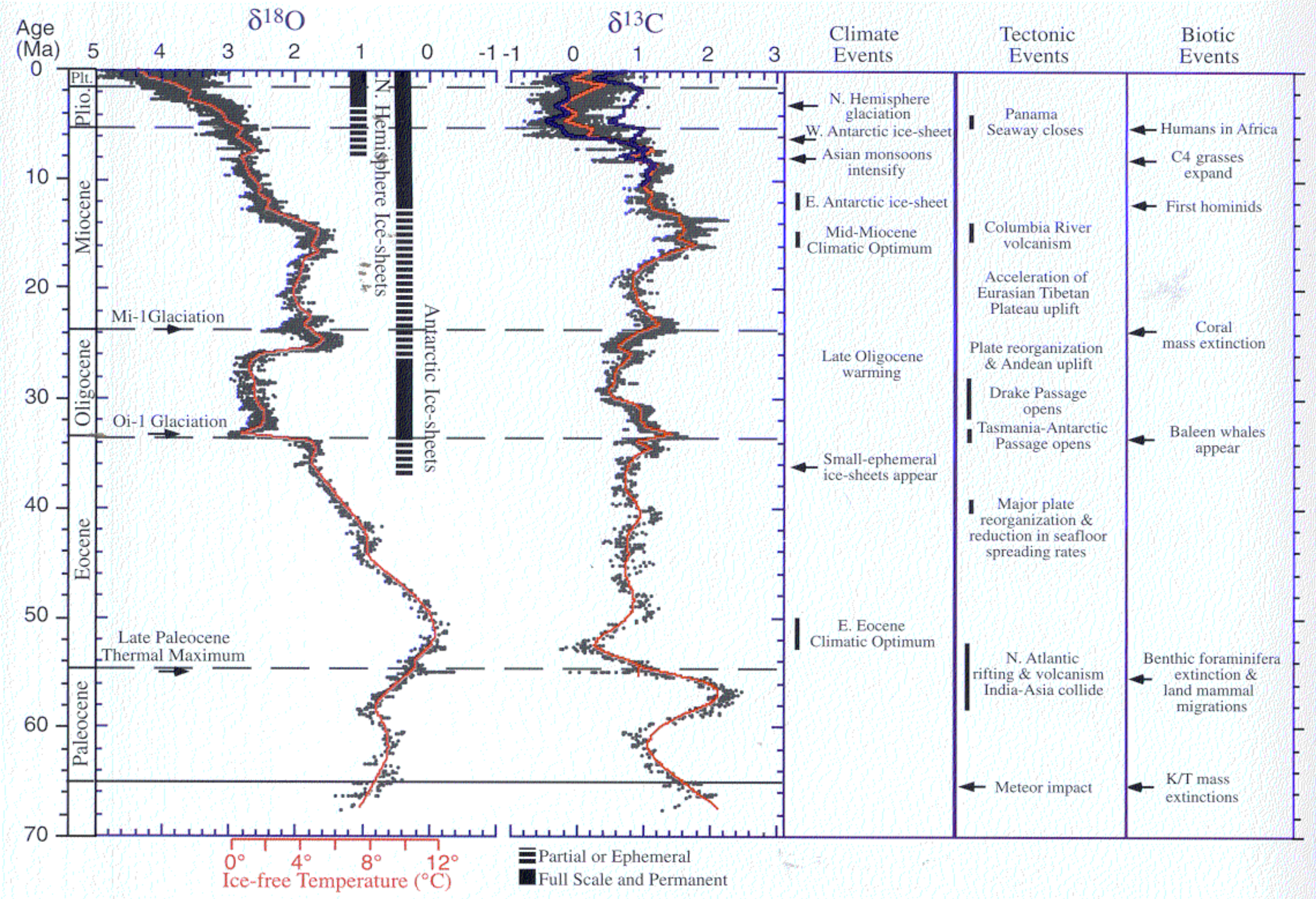


Mackensen & Schmiedl 2019

Global changes in $\delta^{13}C_{DIC}$ of seawater were controlled by CO_2 exchange between the Ocean and other reservoirs with a different carbon isotope composition.

Exchange of carbon between the Lithosphere and the Ocean
Exchange of carbon between the Ocean and the Atmosphere
Transfer of carbon between the Ocean and the Biosphere

Regional changes in $\delta^{13}C_{DIC}$ of seawater were controlled by CO_2 exchange between ocean basins or from one region to another within the same basin

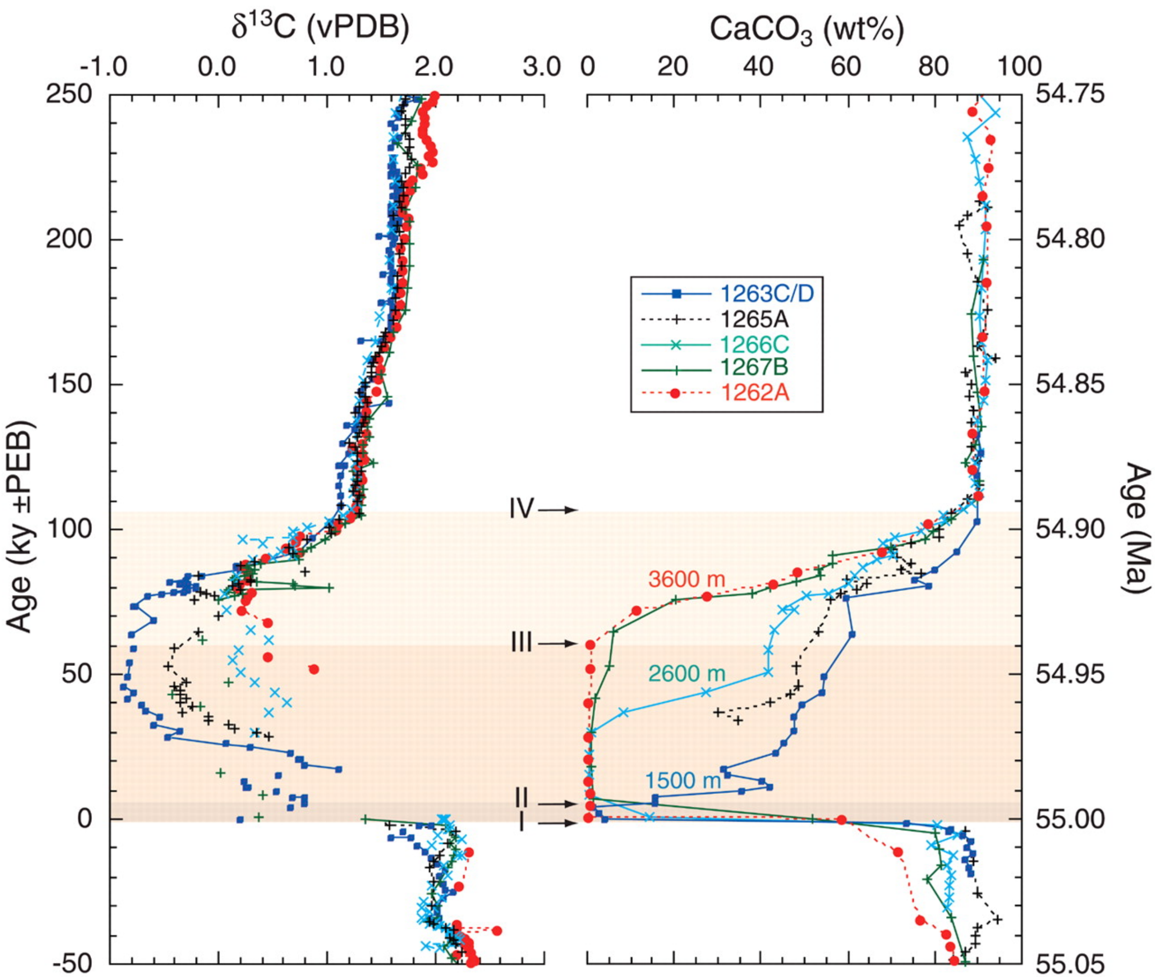


d18O record from the K/T boundary to the Holocene. During the Cretaceous Paleocene and Eocene there was no ice on Earth. The Greenhouse Earth. Near the Eocene-Oligocene boundary, ice started to accumulate in Antartida. This was the onset of the Icehouse Earth. In the Mid Pliocene ice sheets also spread in the northern Hemisphere.

Zachos

Paleocene-Eocene Thermal Maximum (PETM)

Maximum carbon injection into the atmosphere. Release of >4500 GtC
Global warming of 5-8ºC. Ocean acidification. Negative $\delta^{13}C$ excursion
Massive carbonate undersaturation in the deep sea. Extinction of benthic foraminifera



Bacterially produced methane=-60‰
Thermogenic methane = -30 -20‰

Zachos et al. 2005

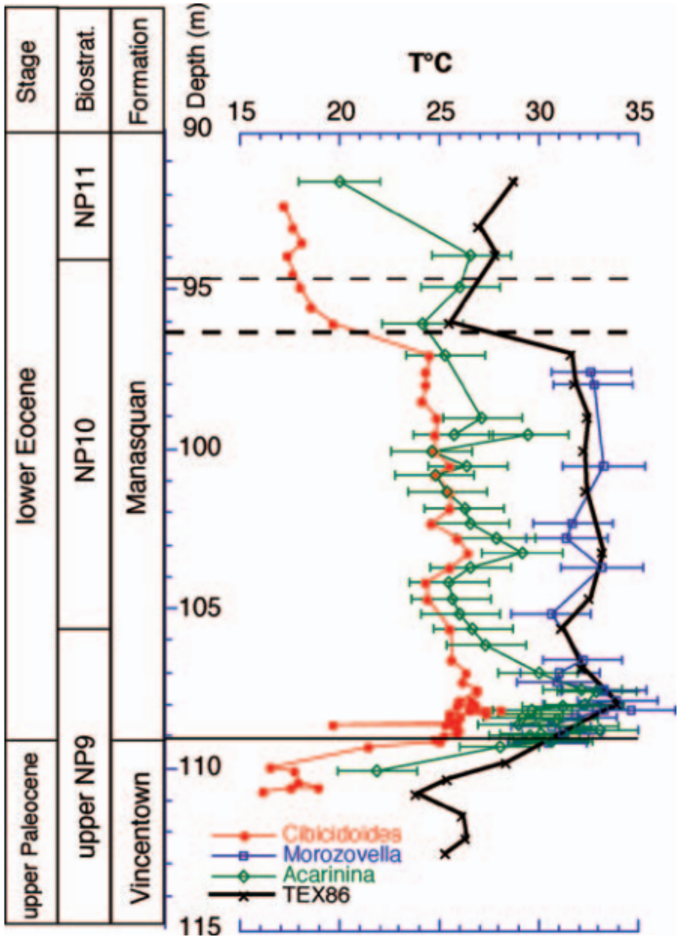
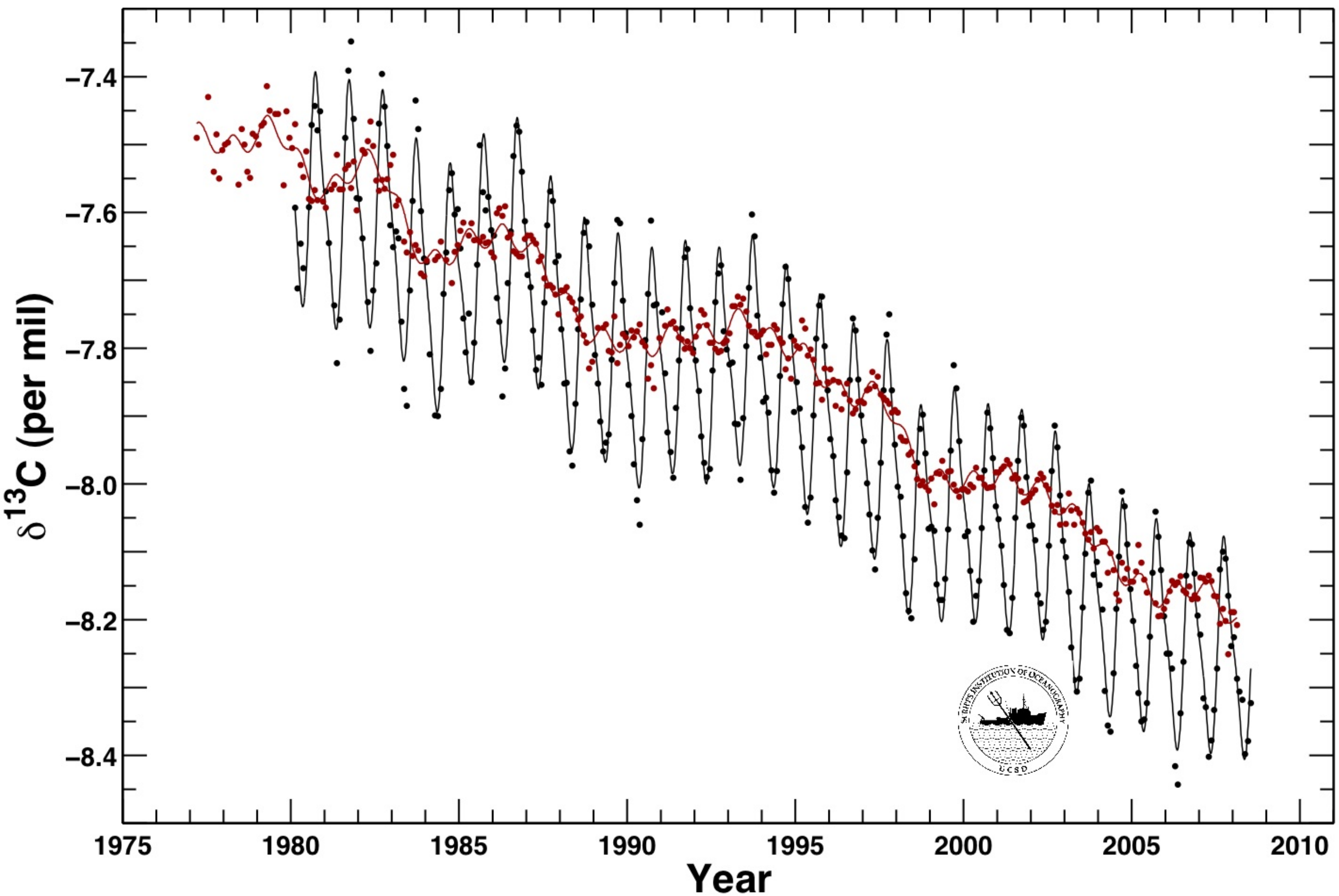


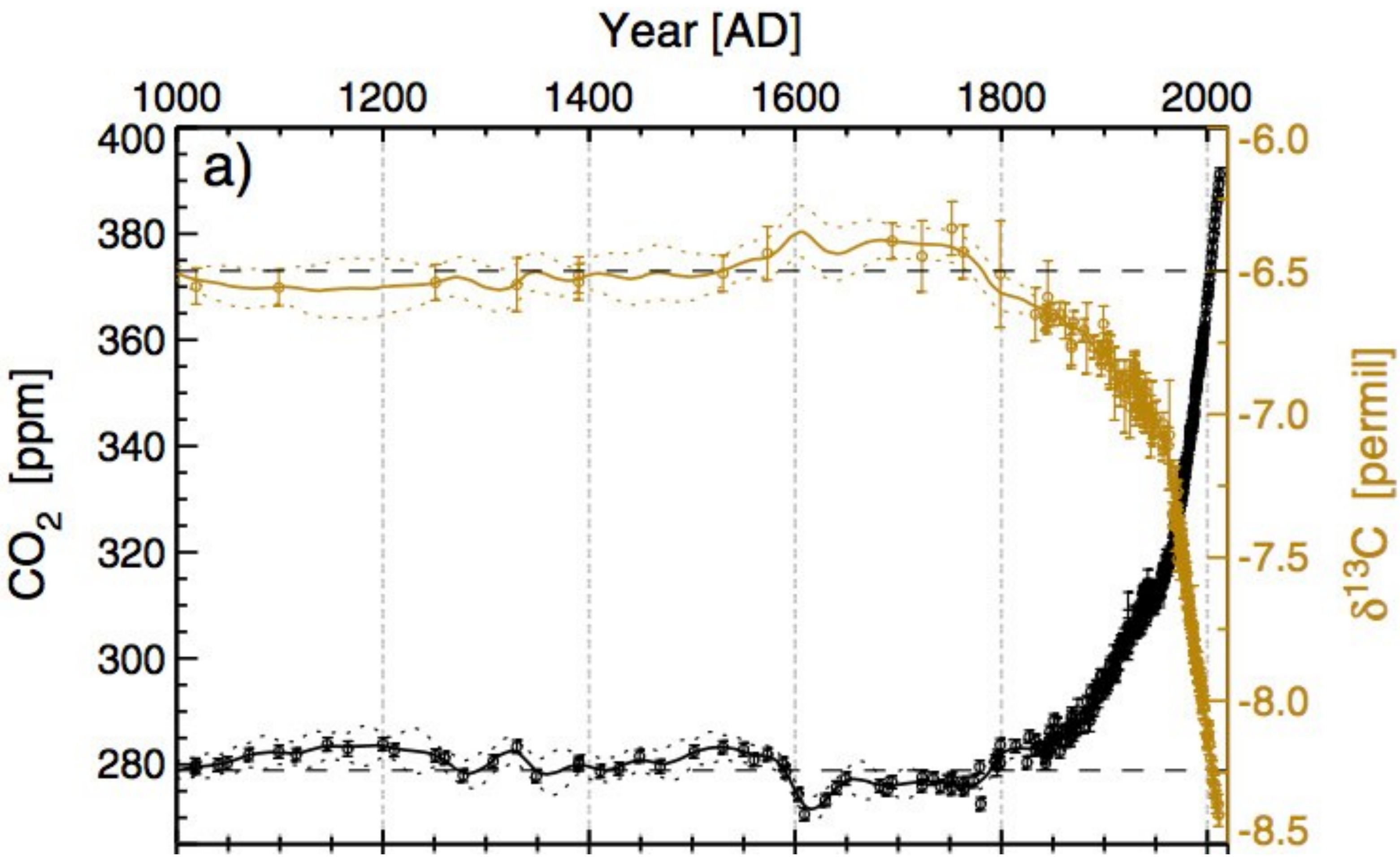
Figure 4. Sea surface temperatures as computed from (1) planktonic foraminifera $\delta^{18}O$ and (2) the TEX_{86}. The oxygen isotope–based curves were derived assuming seawater $\delta^{18}O_{sw}$ of −0.5‰ (SMOW) using standard paleotemperature equation (Erez and Luz, 1983). The errors bars on the planktonic foraminifera curves reflect the range of estimated temperatures associated with just a ±0.5‰ uncertainty in $\delta^{18}O_{sw}$.

Zachos et al. 2006

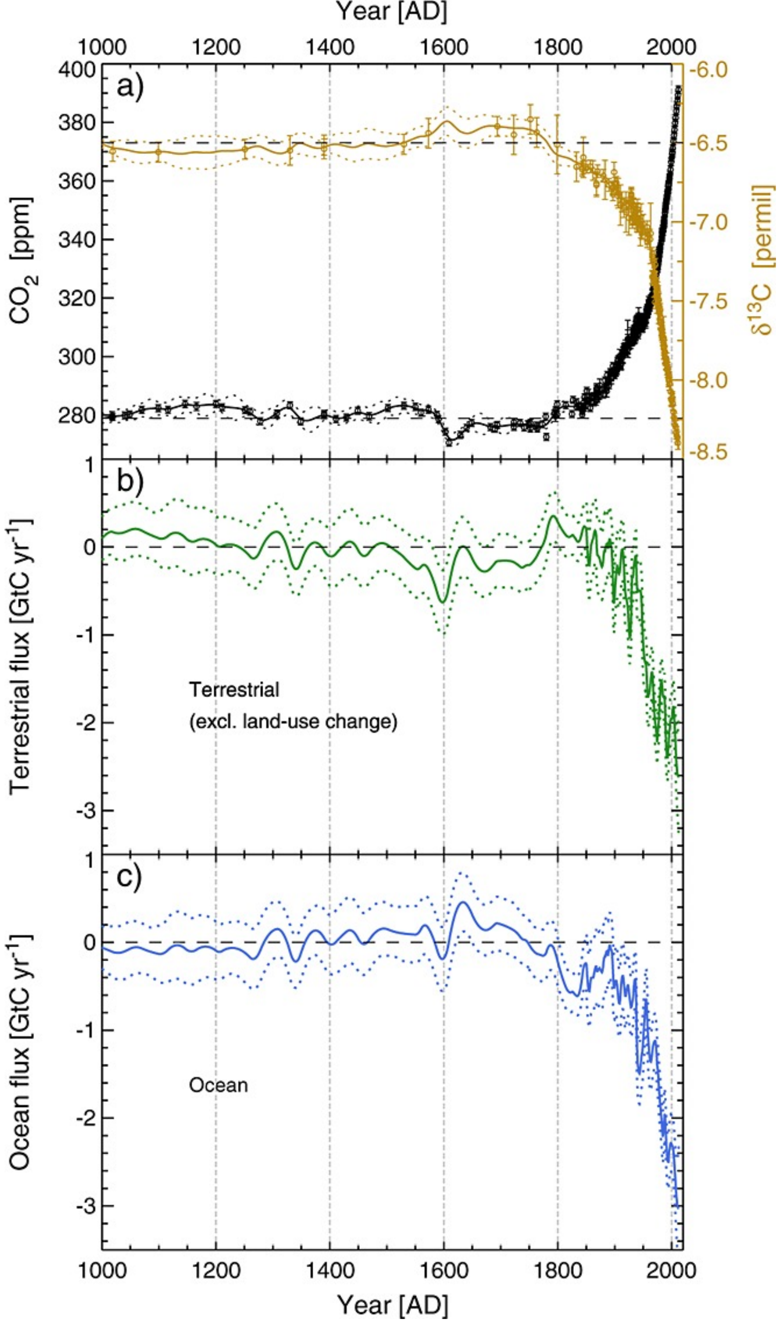
Mauna Loa Observatory, Hawaii and South Pole, Antarctica
Monthly Average Carbon Isotopic Trends

Data from Scripps CO_2 Program   Last updated March 2009





Rubino et al. 2013

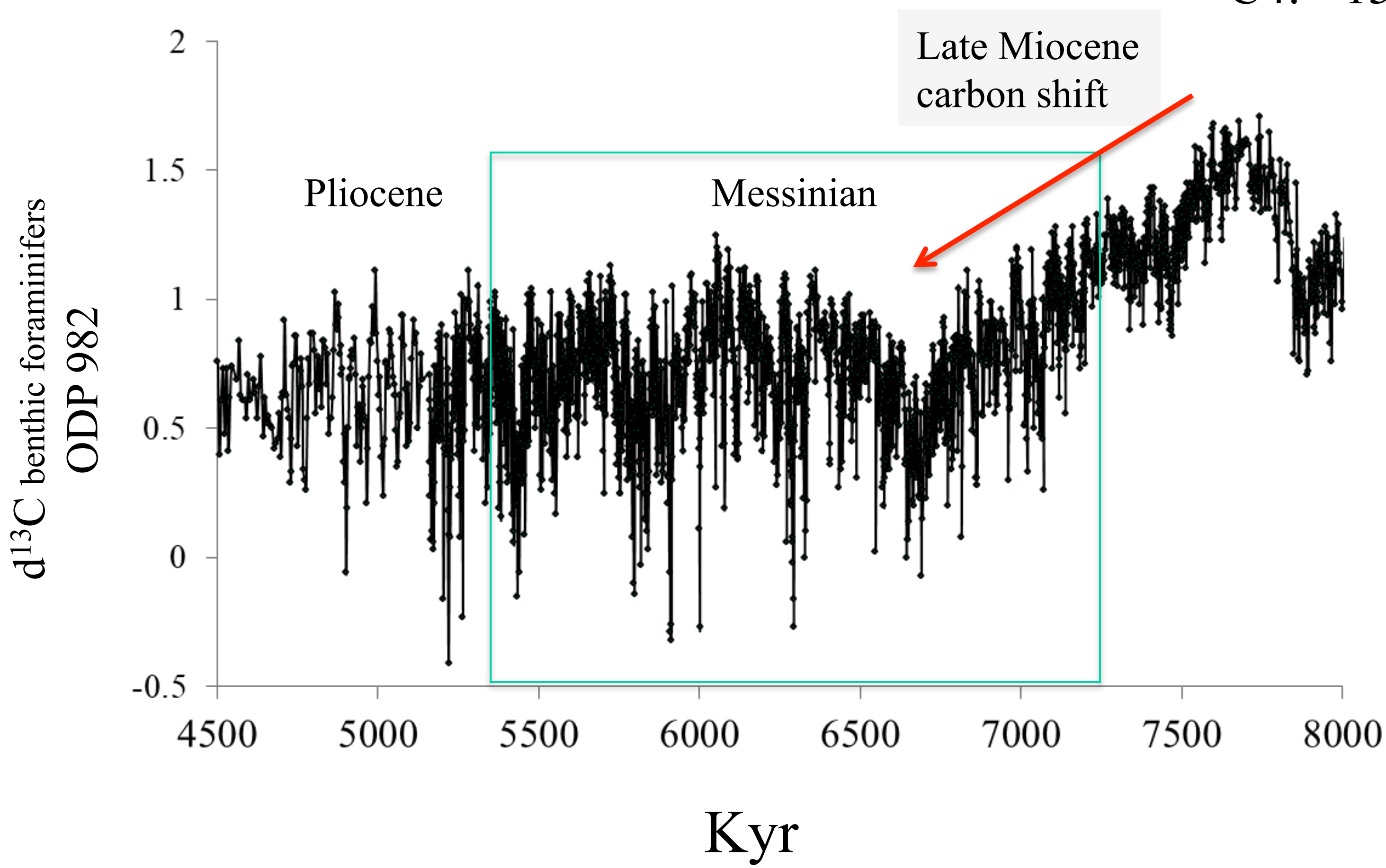


Rubino et al. 2013

Expansion of C4 photosynthesis pathway (higher photosynthetic efficiency) versus C3 photosynthesis

C3: -20‰ -37‰

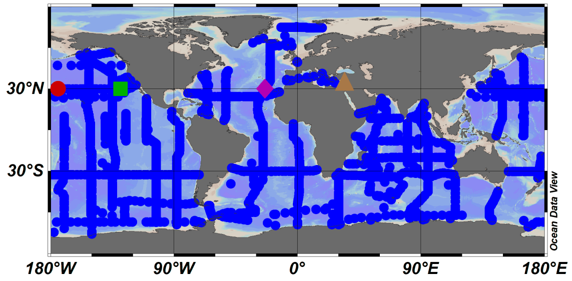
C4: -13‰ -16‰

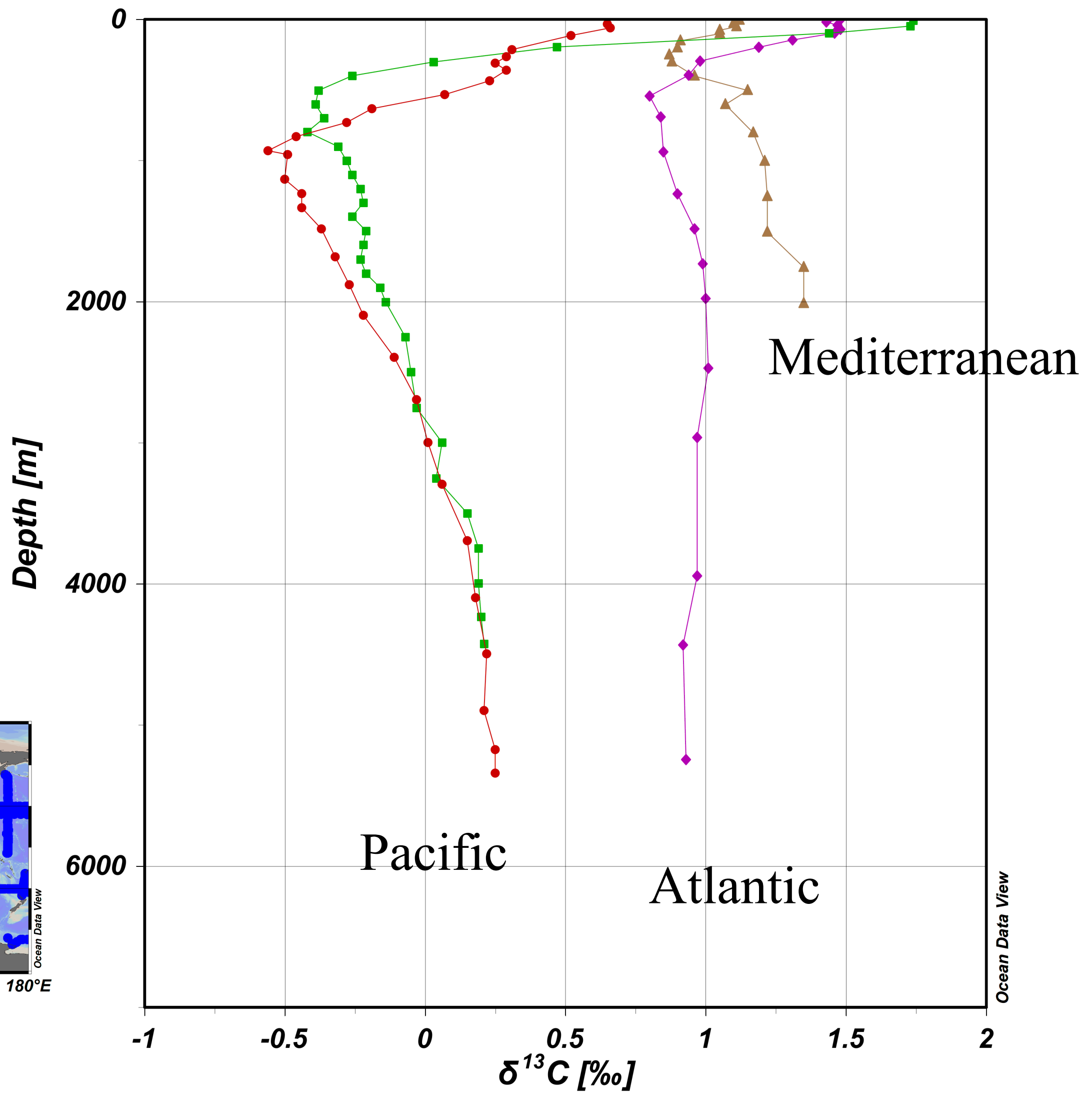


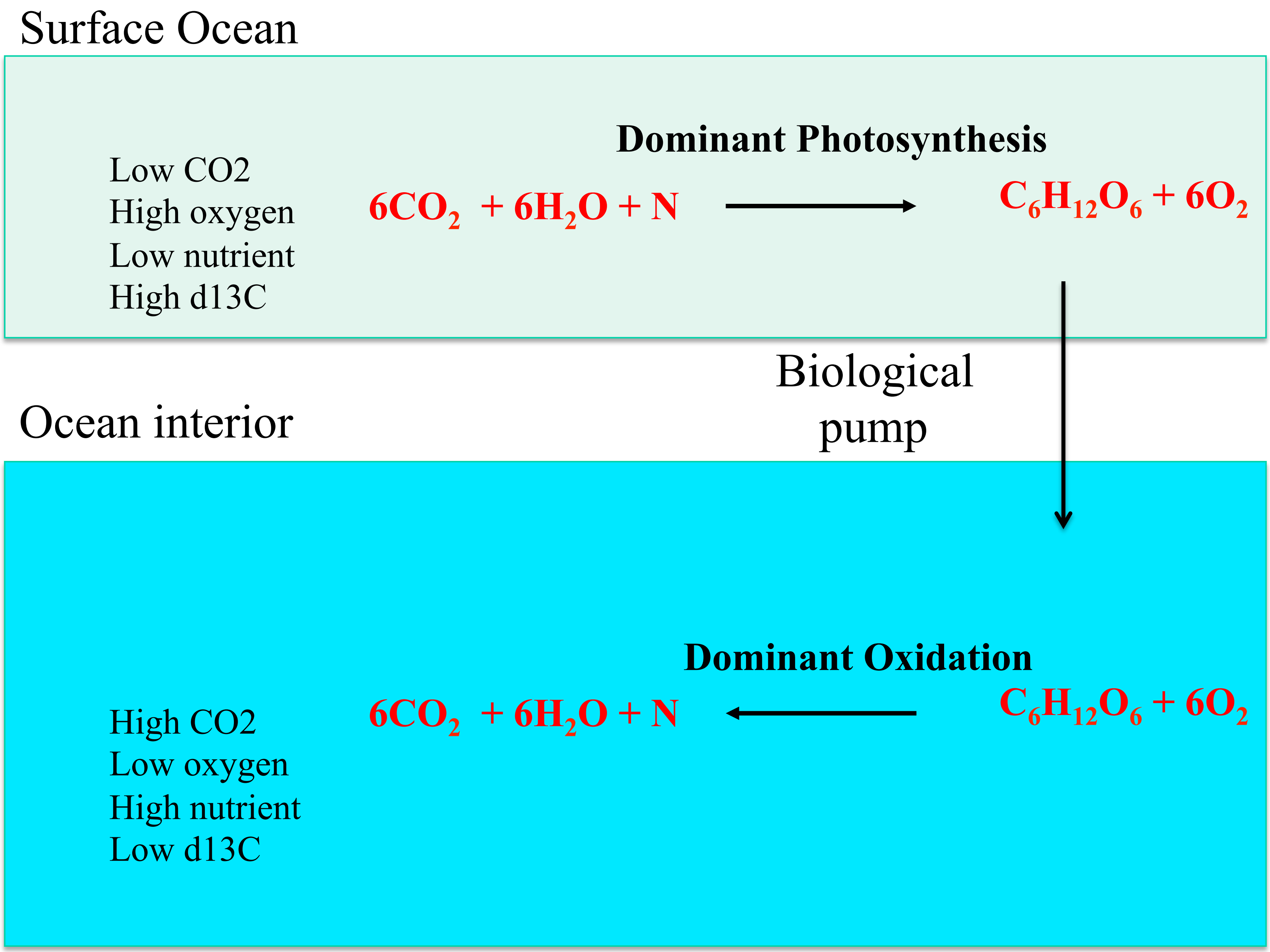
Drury et al. 2018

Regional changes in $\delta^{13}C_{DIC}$

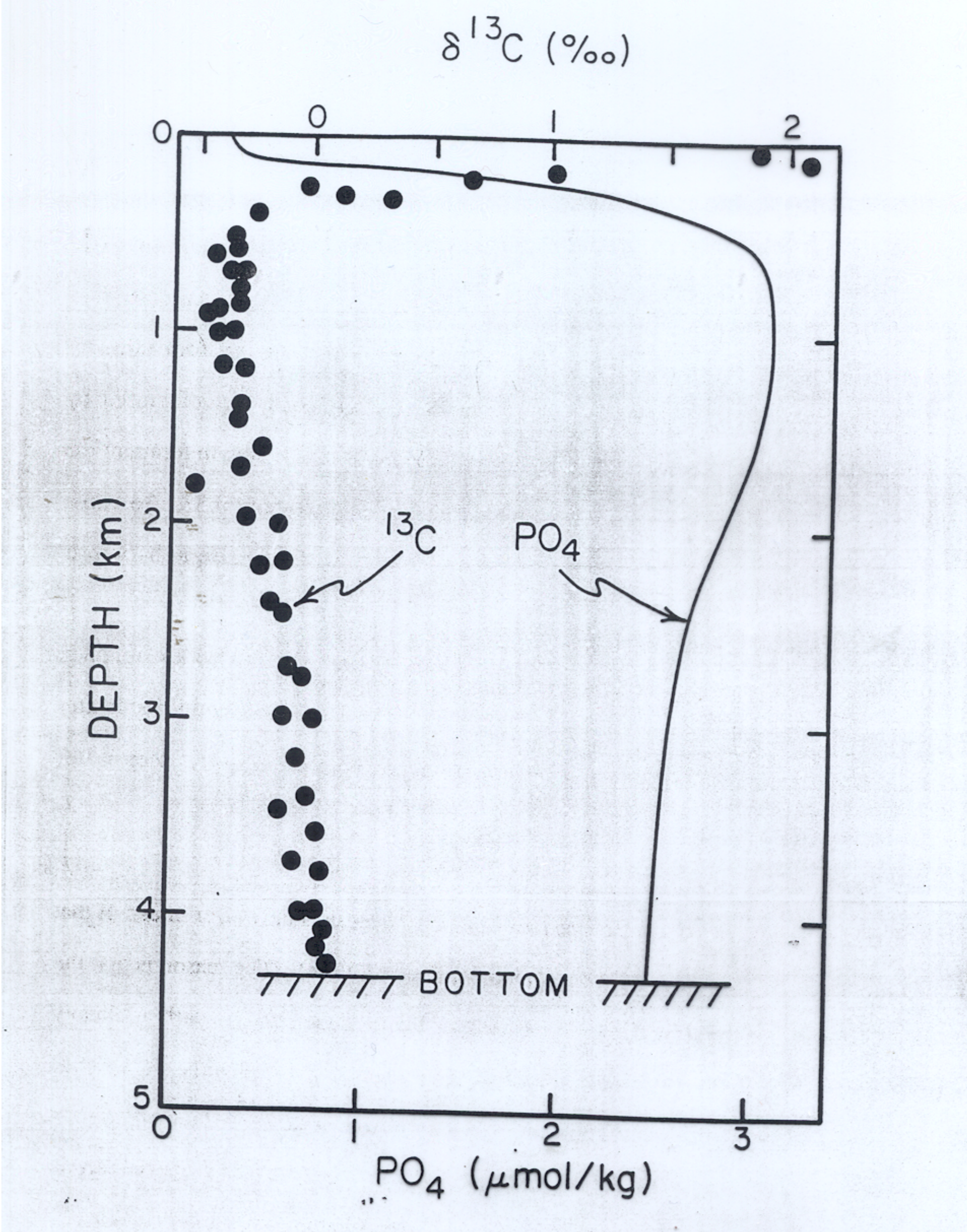
CO_2 exchange between the surface and deep Ocean. ^{12}C is preferentially removed from the surface by phytoplanktonc and exported to the deep Ocean





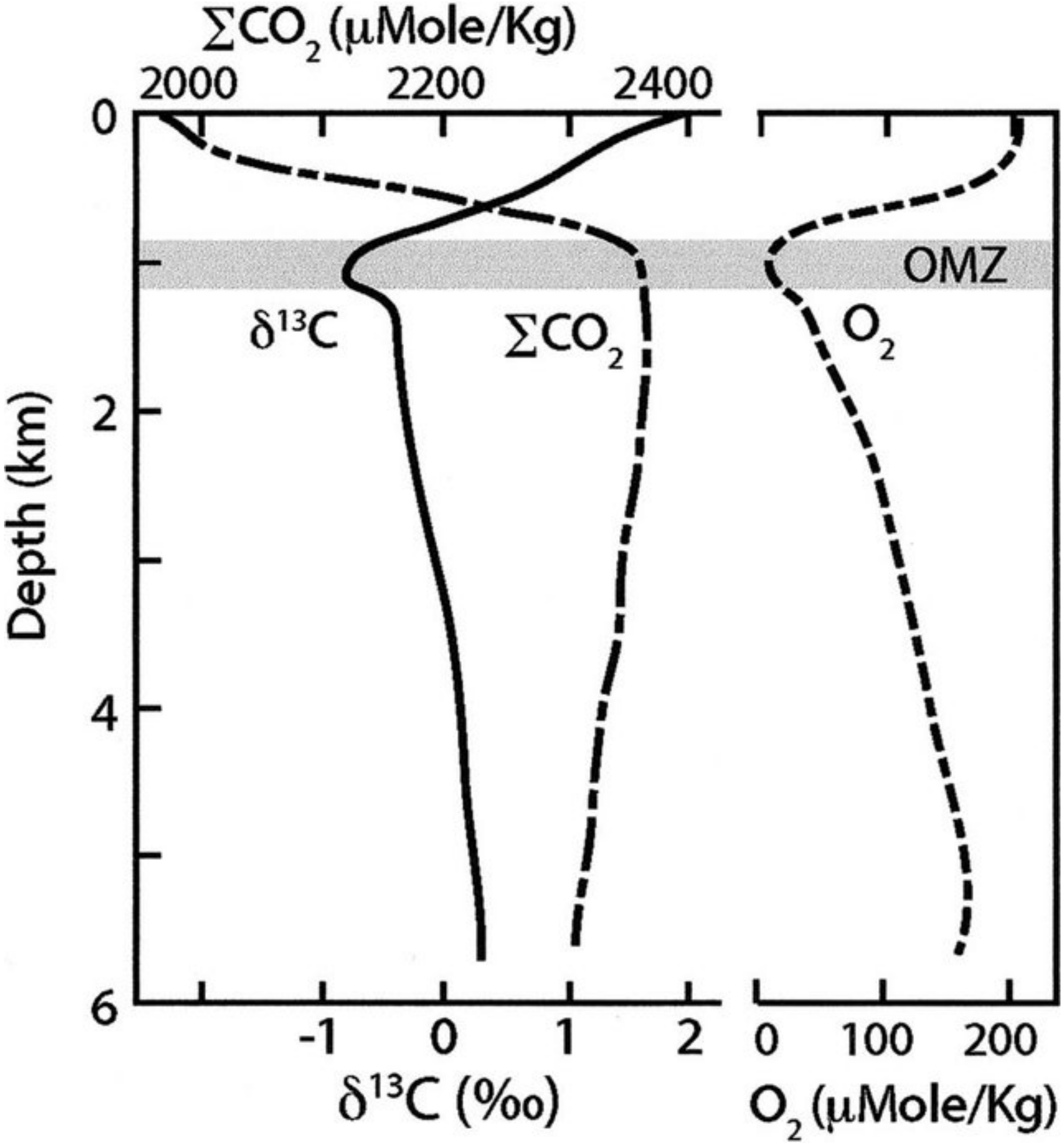


Surface Ocean
Low CO2
High oxygen
Low nutrient
High d13C
Dominant Photosynthesis
$6CO_2 + 6H_2O + N \longrightarrow C_6H_{12}O_6 + 6O_2$
Biological pump
Ocean interior
Dominant Oxidation
$6CO_2 + 6H_2O + N \longleftarrow C_6H_{12}O_6 + 6O_2$
High CO2
Low oxygen
High nutrient
Low d13C



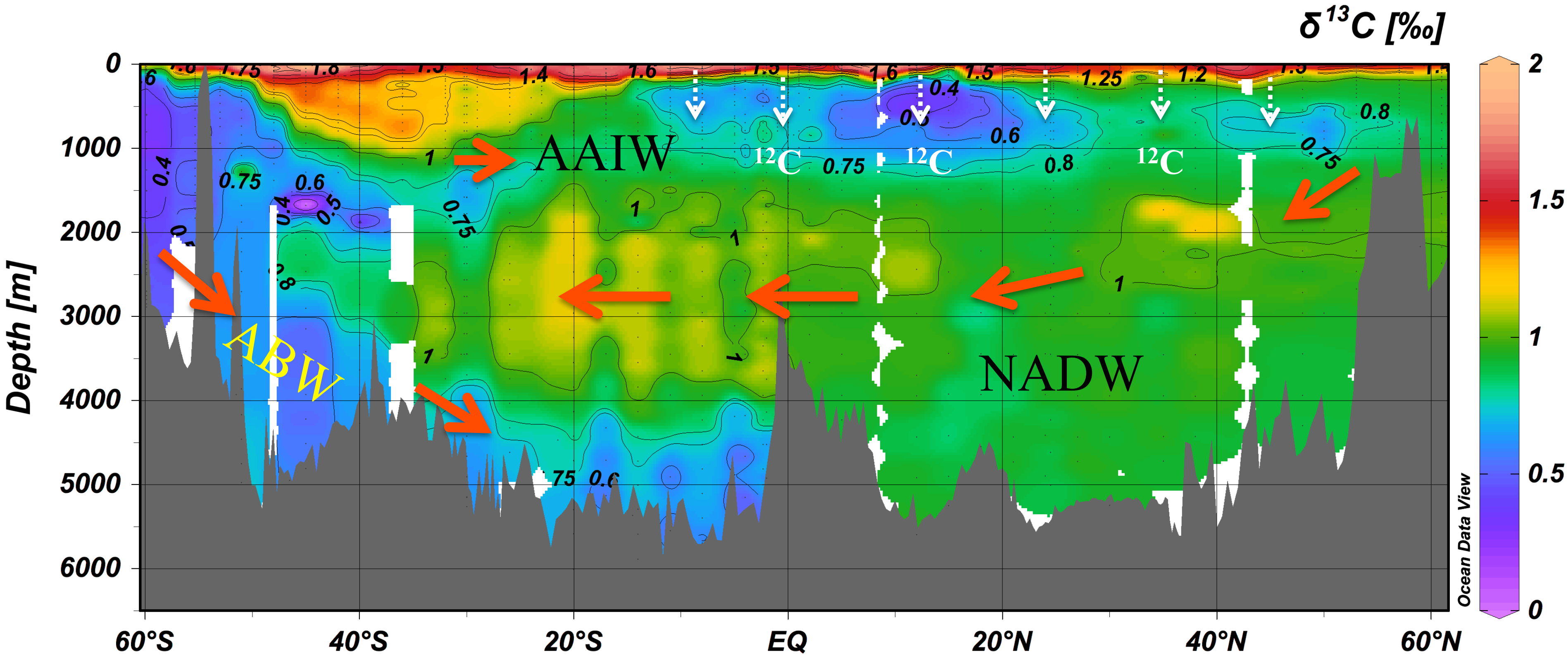
Photosyntheis remove 12C from the surface and and is tranferred to the Ocean interior with the sinking organic matter

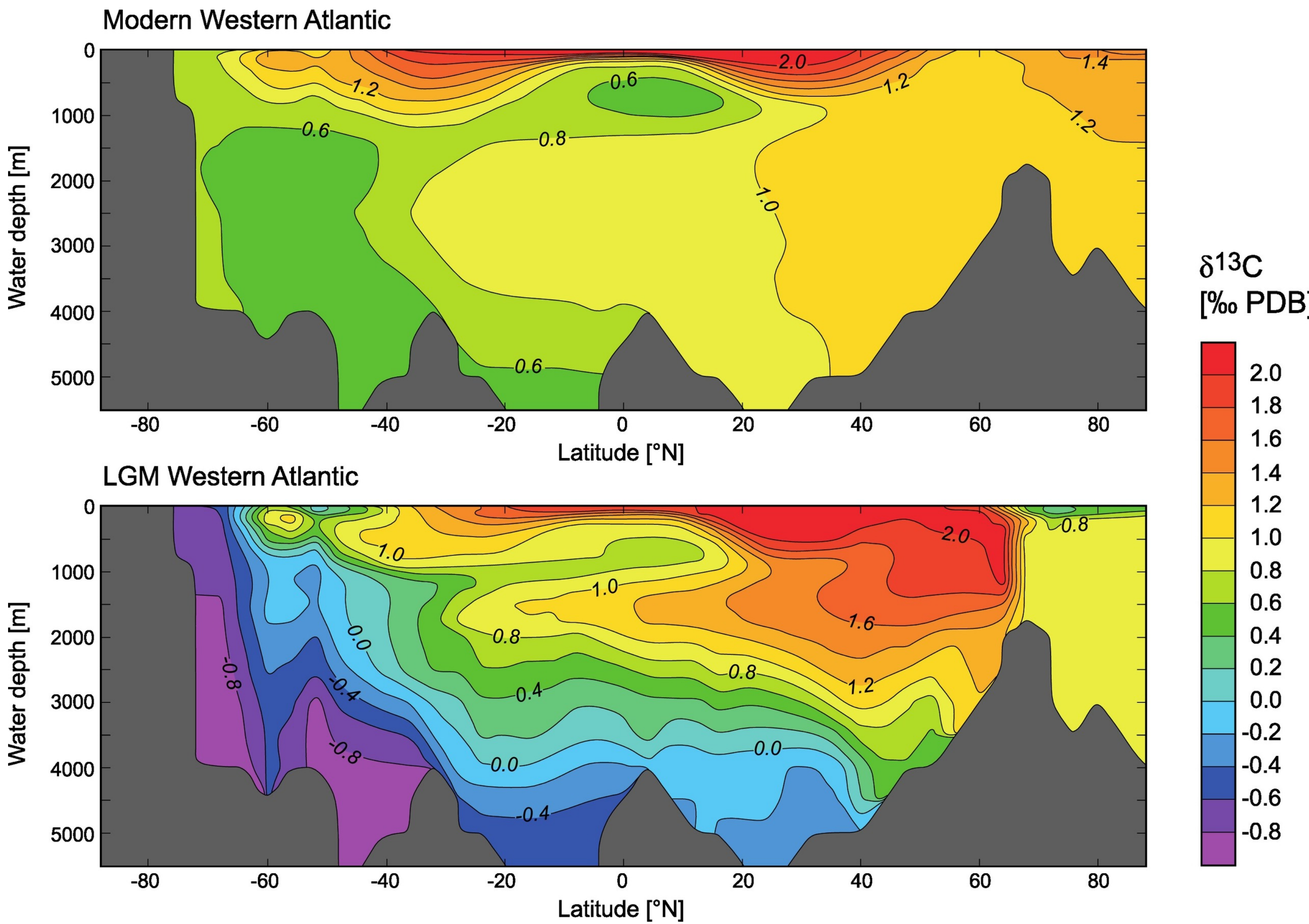
Broecker 1992



ΣCO$_2$ (μMole/Kg)
2000
2200
2400
0
2
4
6
Depth (km)
OMZ
δ^{13}C
ΣCO$_2$
O$_2$
-1
0
1
2
δ^{13}C (‰)
0
100
200
O$_2$ (μMole/Kg)

d^{13}C profile in the Atlantic





Modern Western Atlantic
LGM Western Atlantic
Water depth [m]
Latitude [°N]
0
1000
2000
3000
4000
5000
-80
-60
-40
-20
0
20
40
60
80
2.0
1.4
1.2
0.6
0.8
1.0
0.0
-0.4
-0.8
1.6
0.4
δ13C
[‰ PDB]
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8

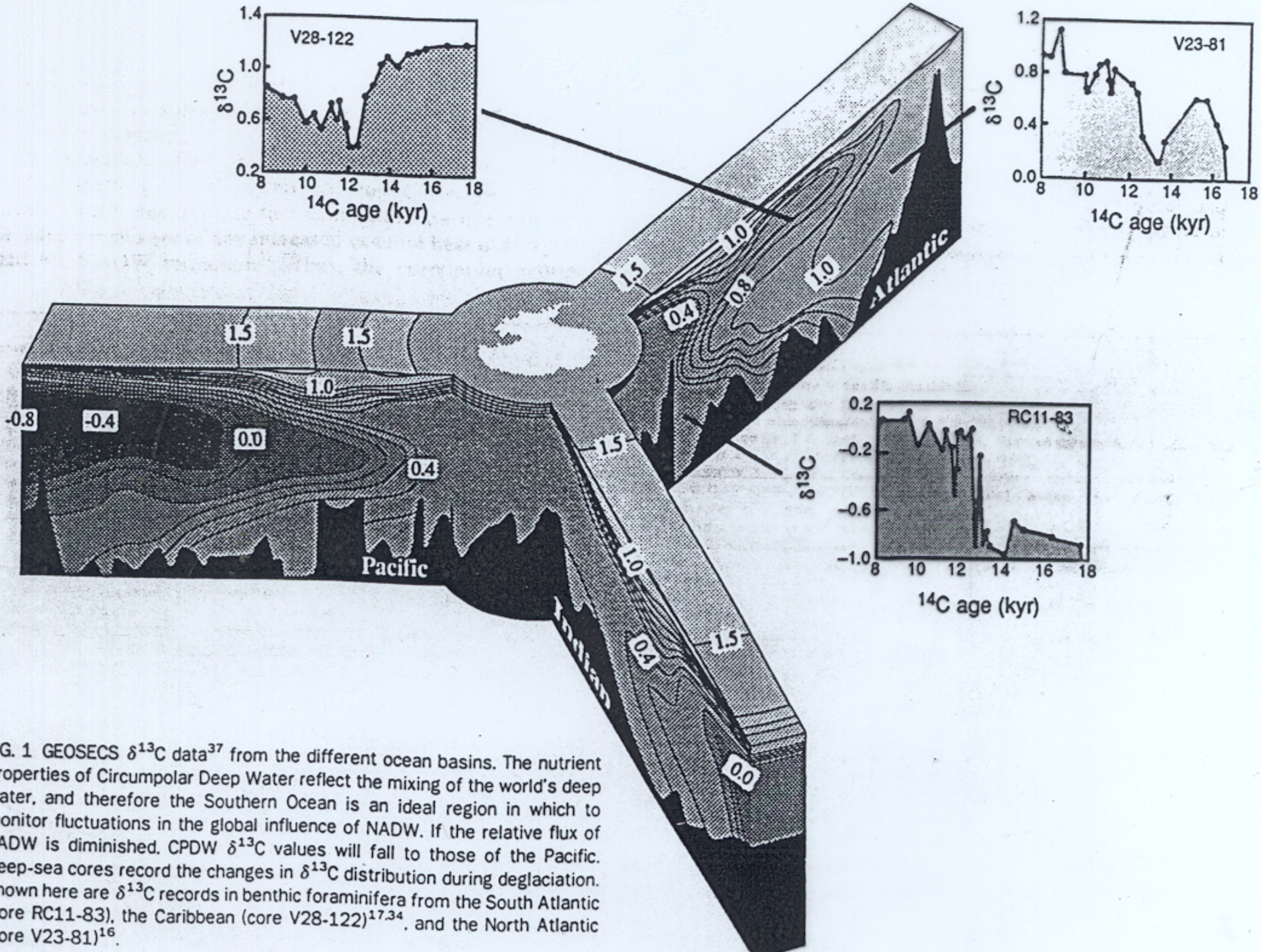
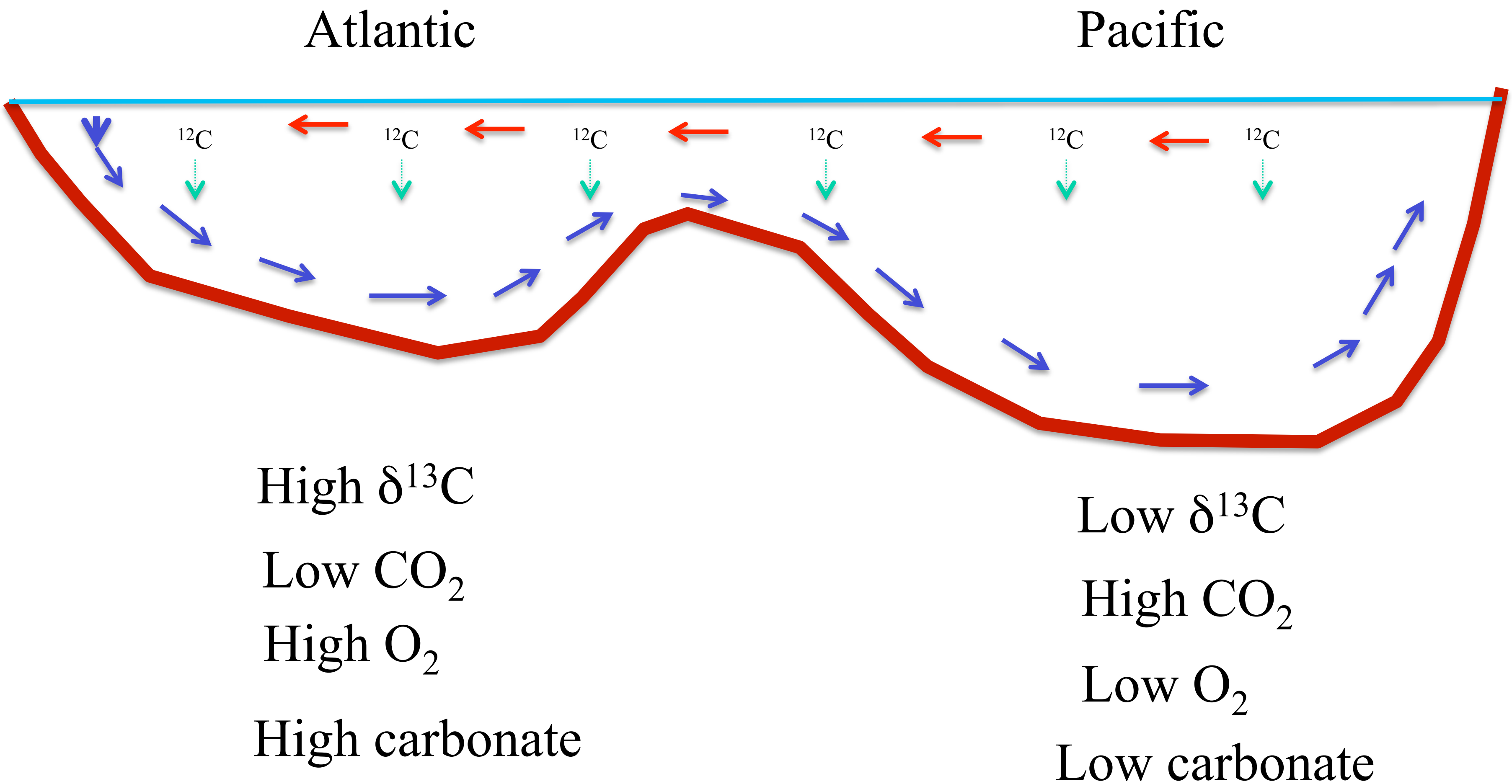


FIG. 1 GEOSECS $\delta^{13}C$ data[37] from the different ocean basins. The nutrient properties of Circumpolar Deep Water reflect the mixing of the world's deep water, and therefore the Southern Ocean is an ideal region in which to monitor fluctuations in the global influence of NADW. If the relative flux of NADW is diminished, CPDW $\delta^{13}C$ values will fall to those of the Pacific. Deep-sea cores record the changes in $\delta^{13}C$ distribution during deglaciation. Shown here are $\delta^{13}C$ records in benthic foraminifera from the South Atlantic (core RC11-83), the Caribbean (core V28-122)[17,34], and the North Atlantic (core V23-81)[16].


Atlantic
Pacific
12C
12C
12C
12C
12C
12C
High δ13C
Low CO2
High O2
High carbonate
Low δ13C
High CO2
Low O2
Low carbonate