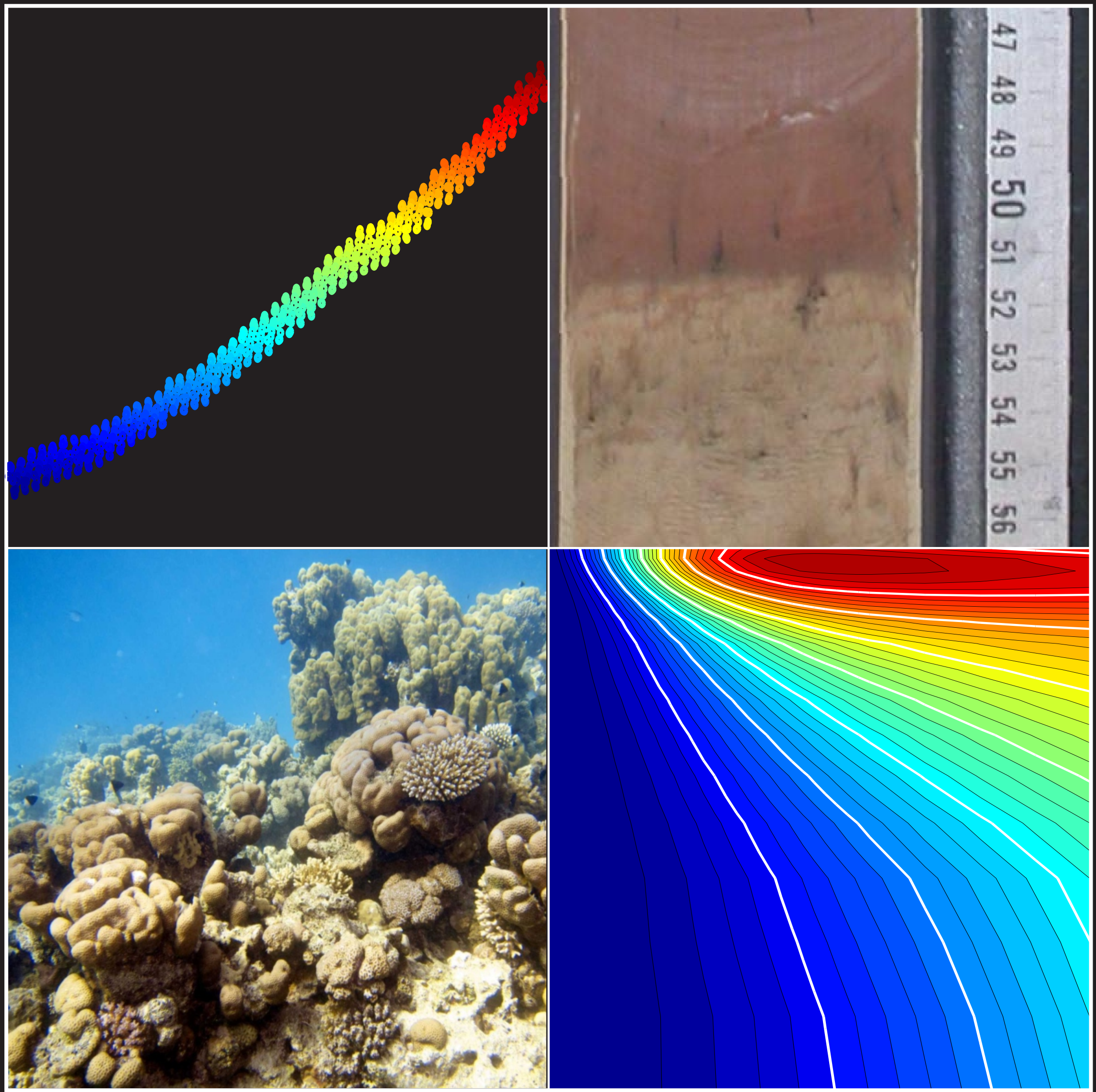
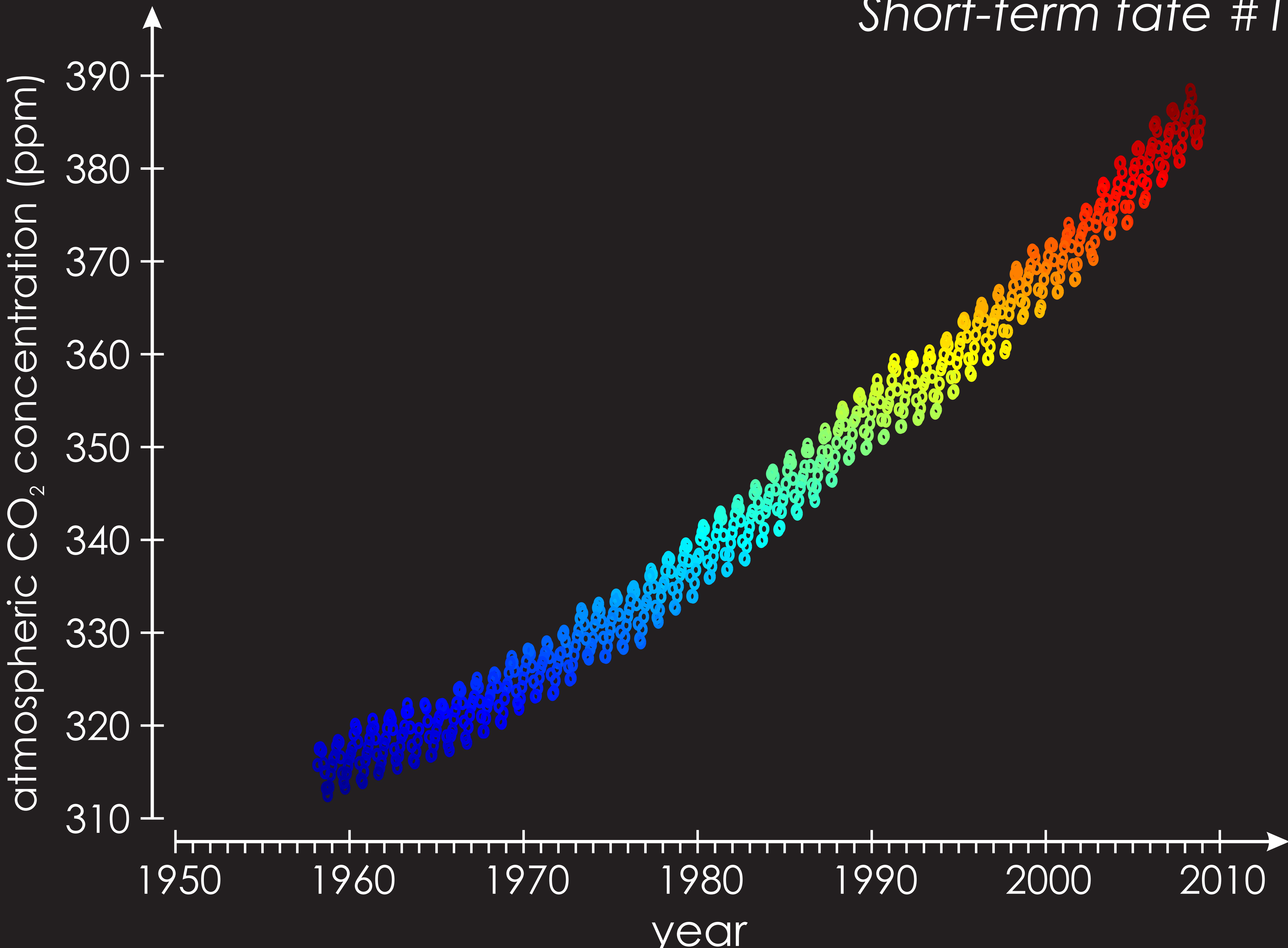
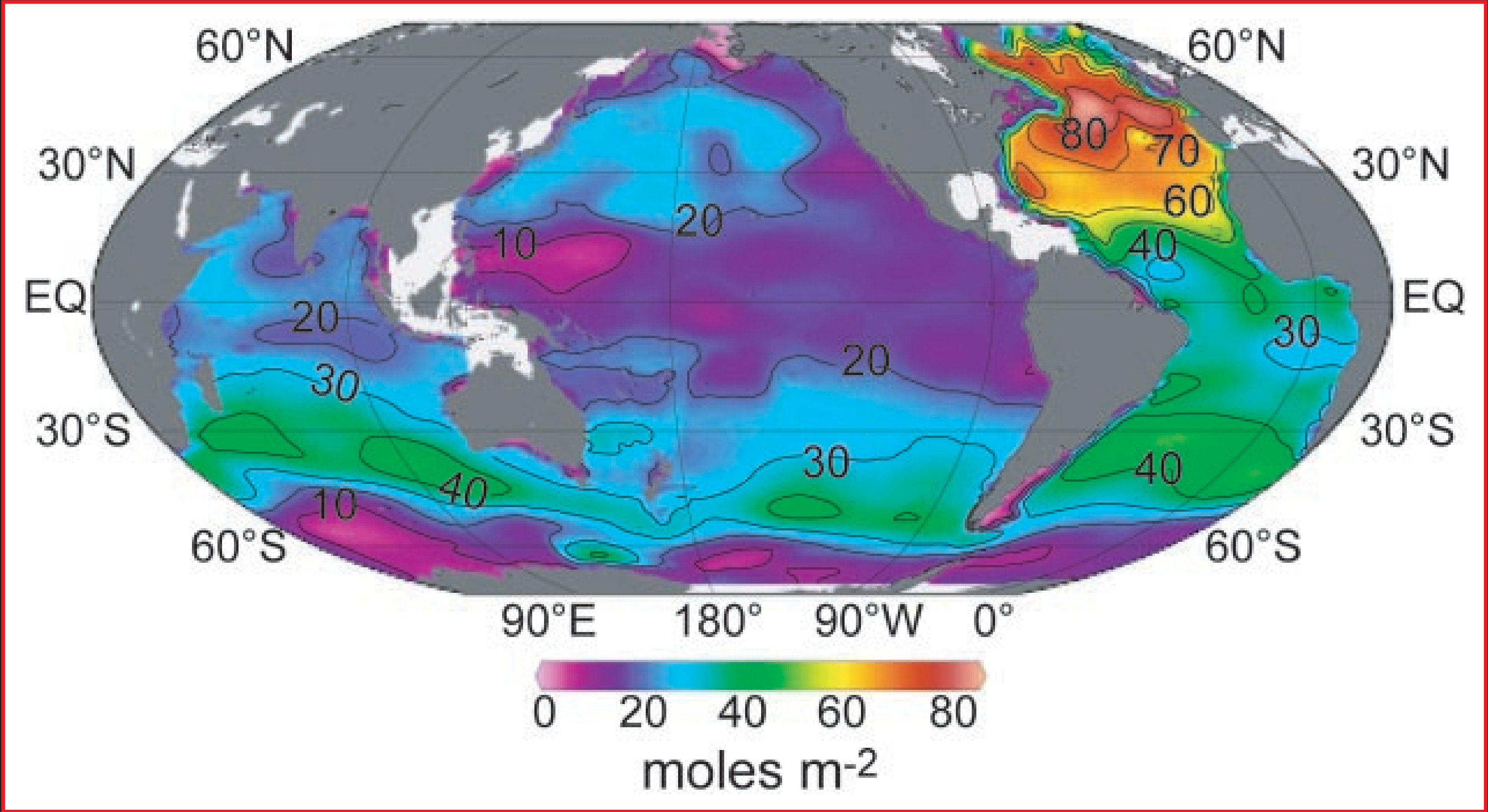
The long-term fate of fossil fuel CO_2



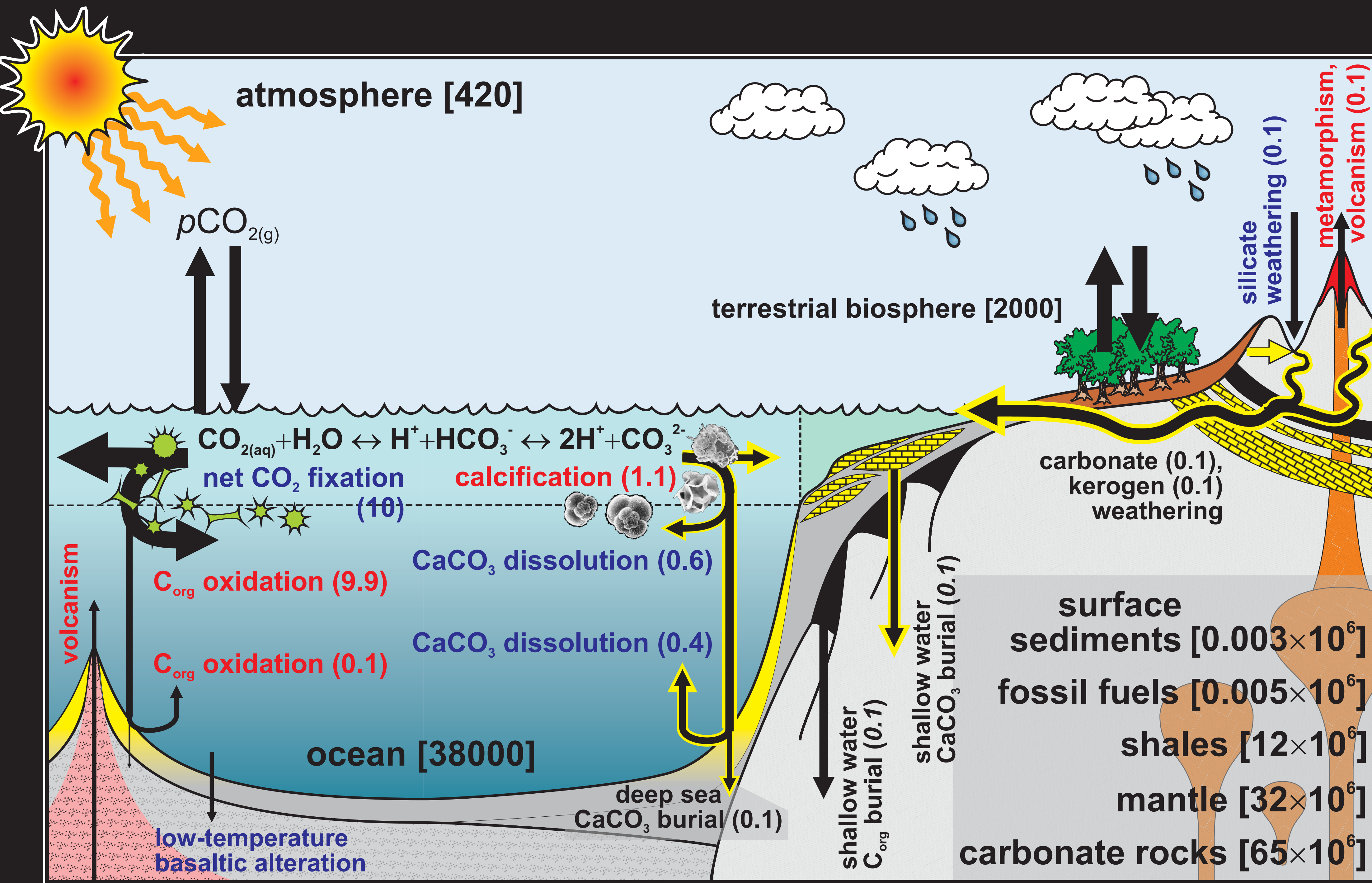

Short-term fate #1
atmospheric CO_2 concentration (ppm)
390
380
370
360
350
340
330
320
310
1950
1960
1970
1980
1990
2000
2010
year

Short-term fate #2

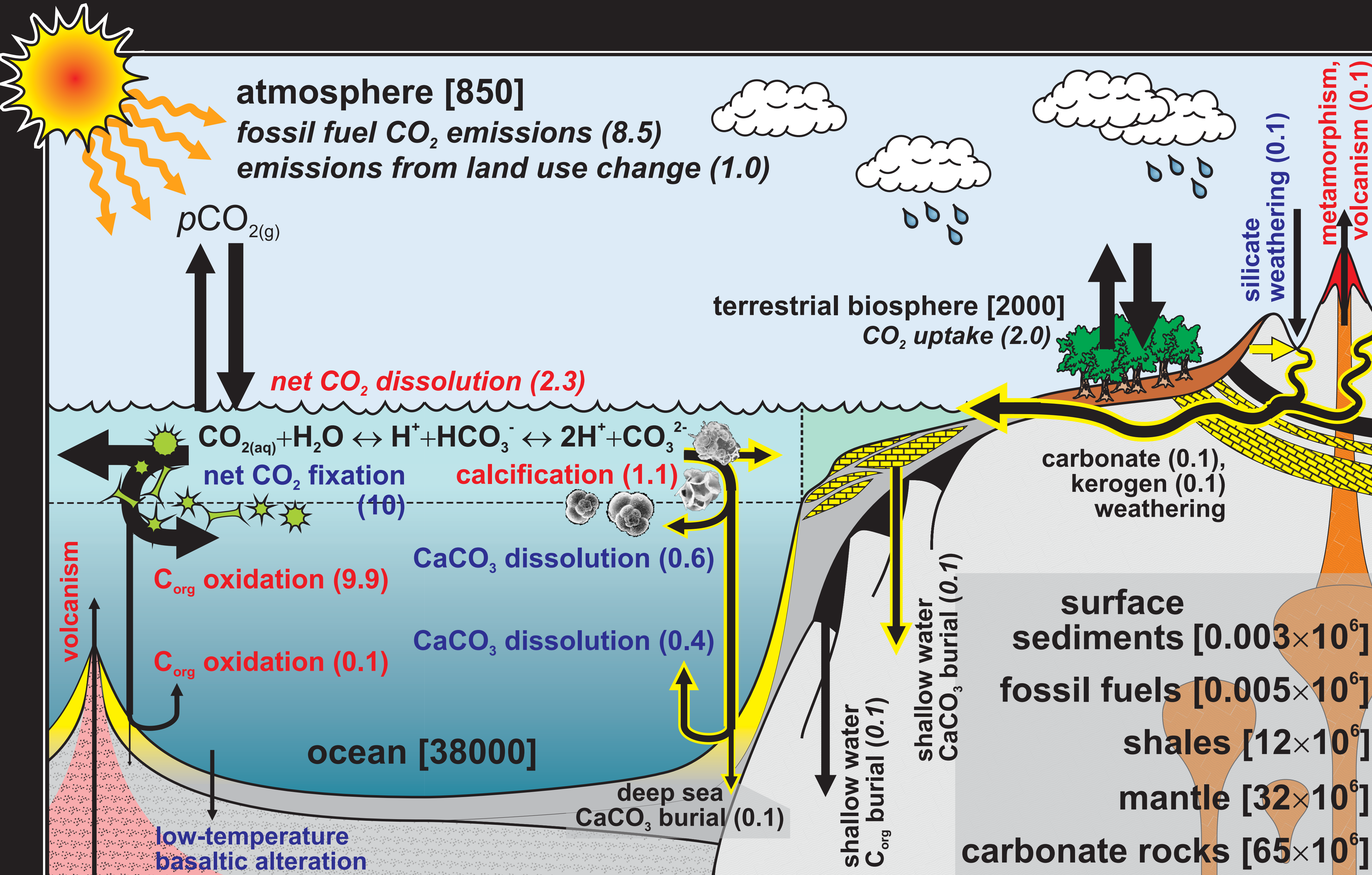


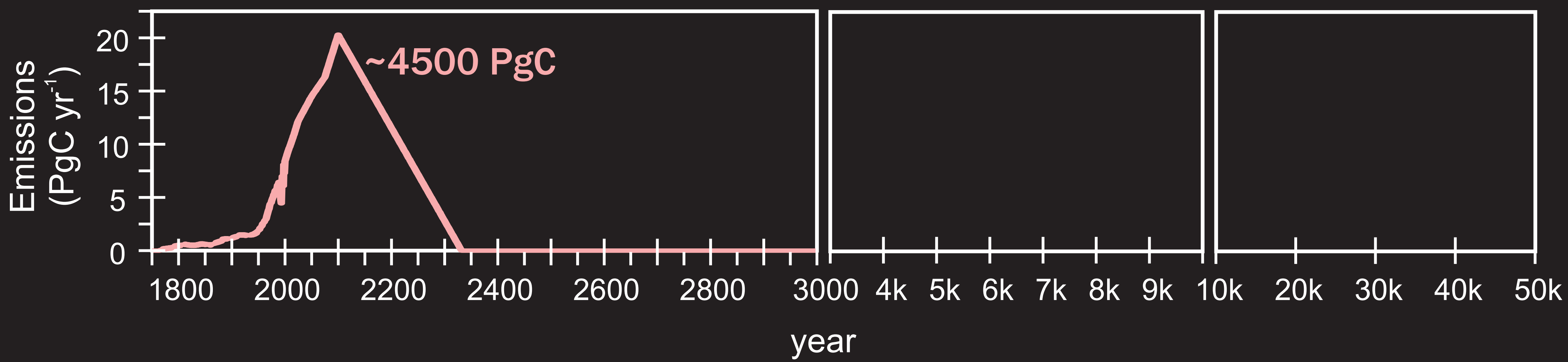
From: *Sabine et al.* [2004] (*Science* 305)

The global carbon cycle: 'natural'



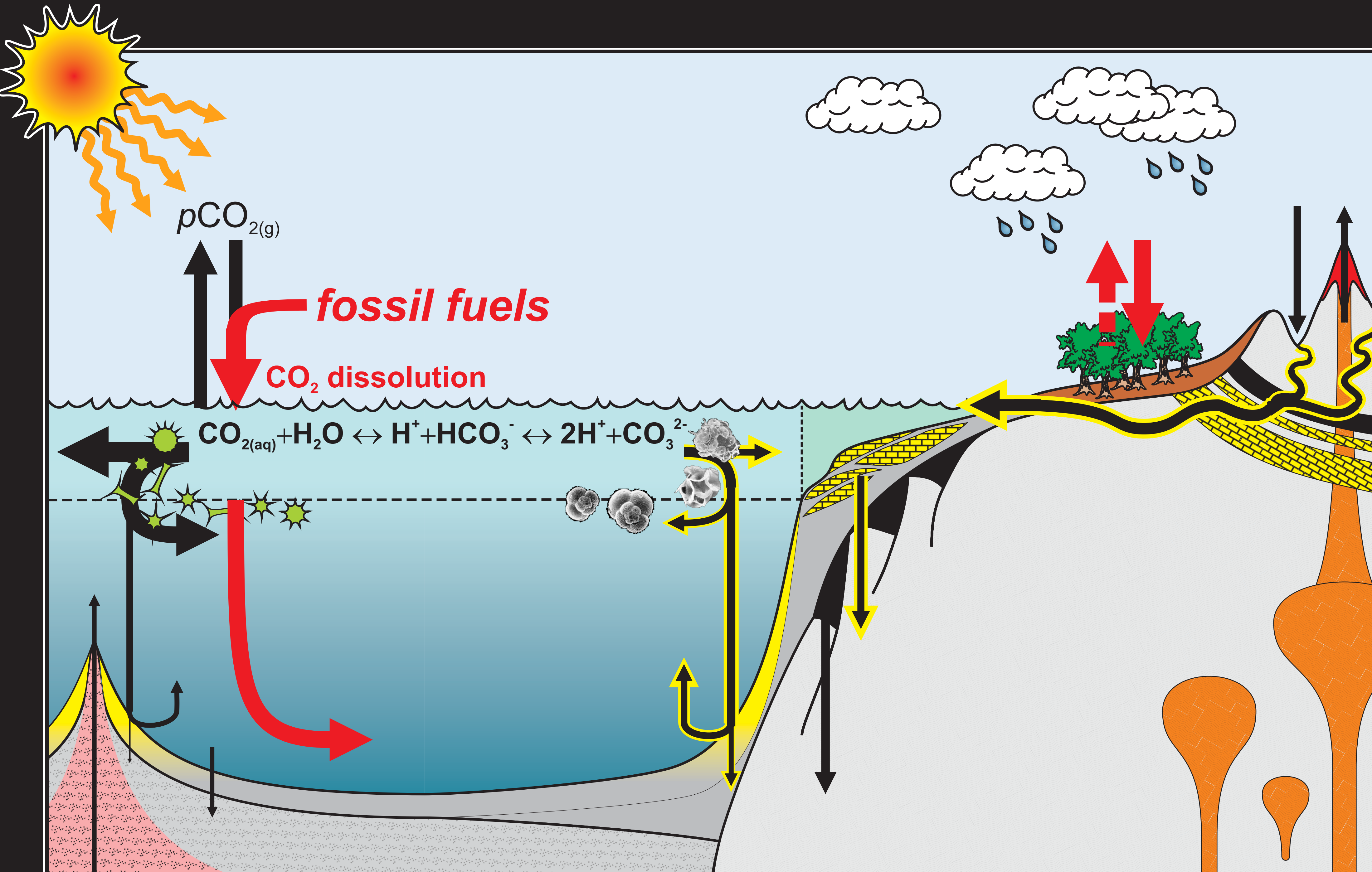
The global carbon cycle: modern





From: *Ridgwell and Hargreaves* [2007] (*GBC*)

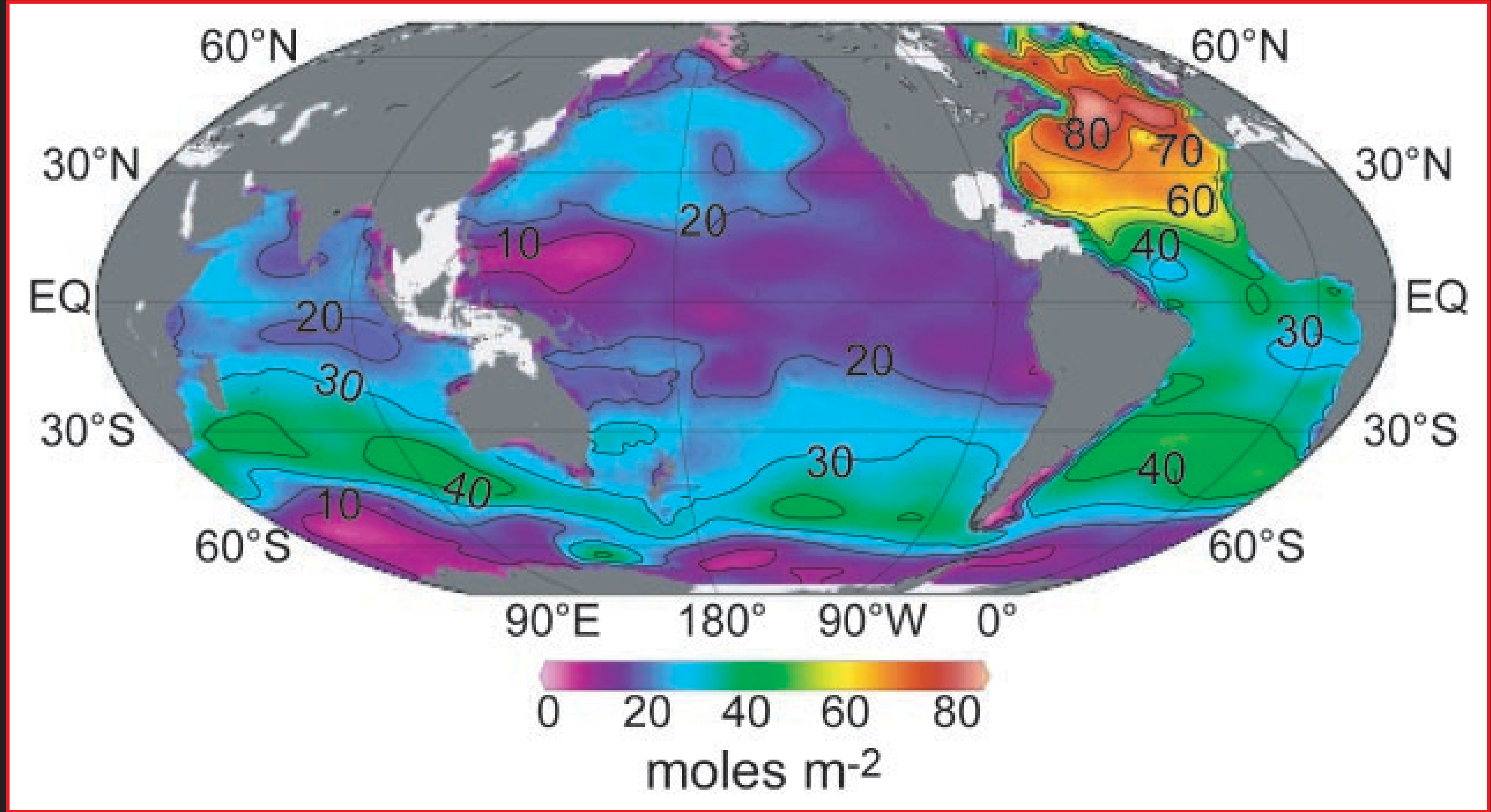
The marine carbon cycle - dynamics



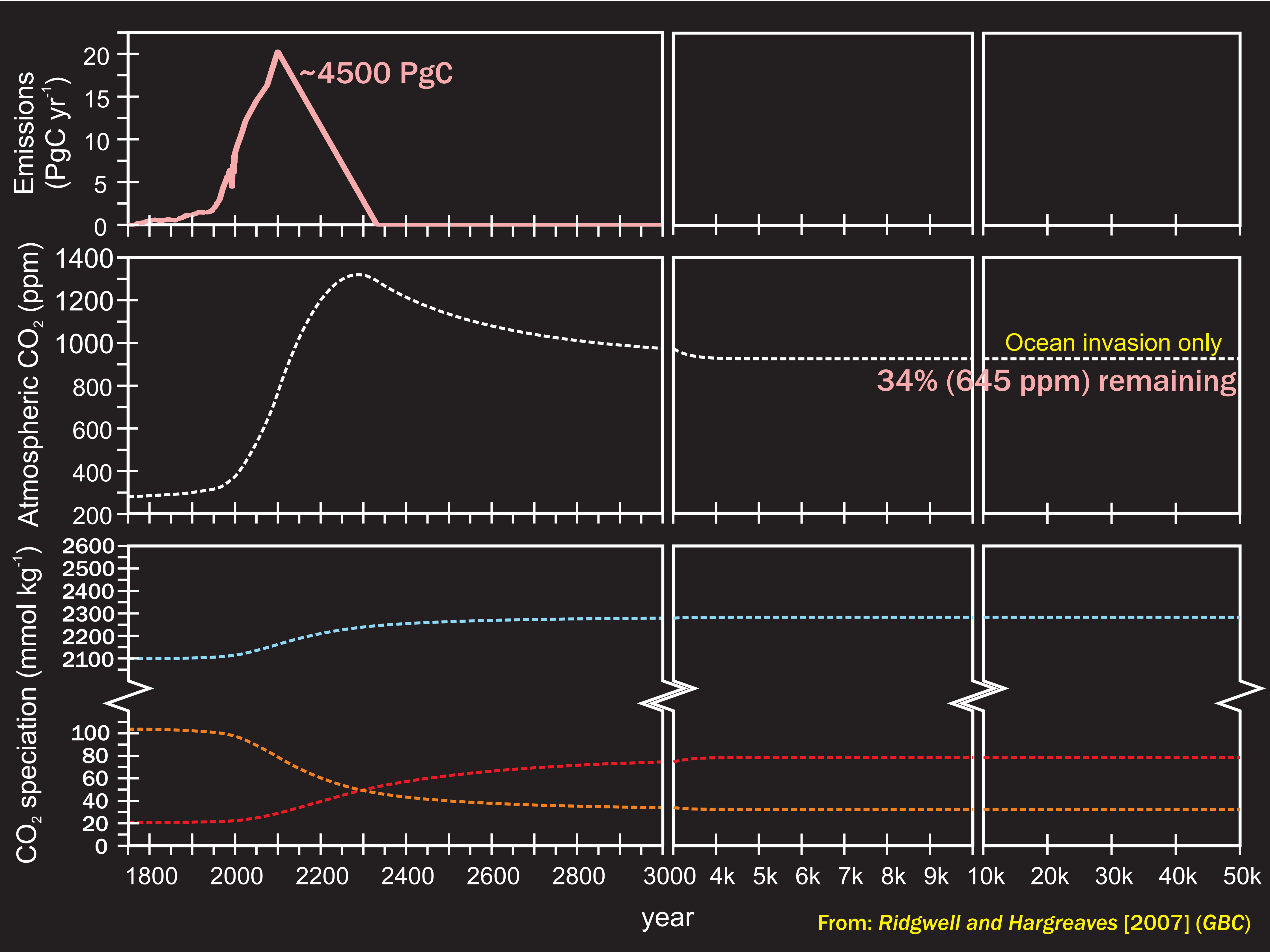
The marine carbon cycle - dynamics

Currently (2000-2005) some 2.2 PgC yr^{-1} CO_2 dissolves in the ocean.

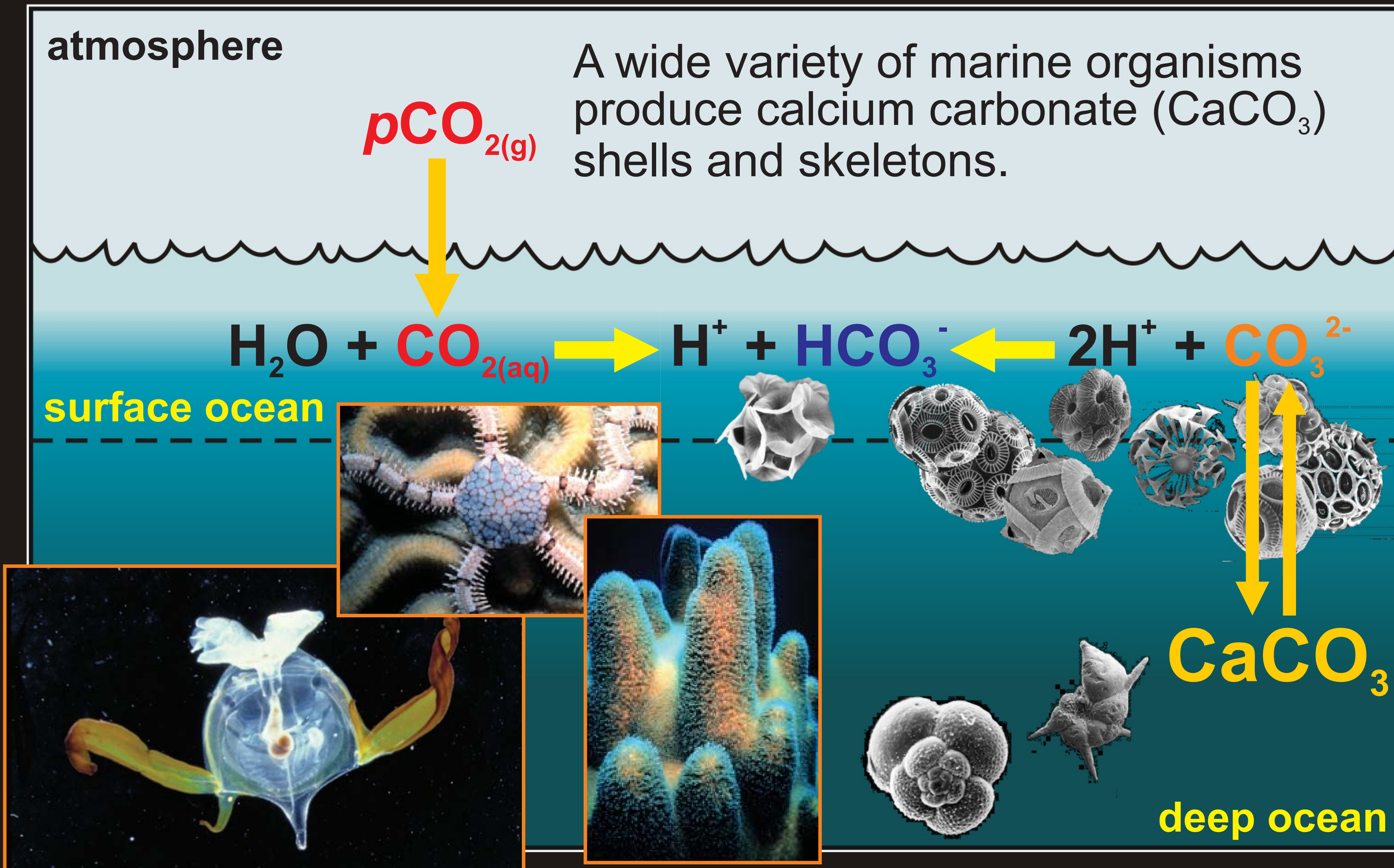
From 1800 to 1994, the ocean has taken up 118±19 PgC (below), accounting for 48% of the total fossil-fuel and cement-manufacturing emissions during that period (or about one third when including releases from land use change) [*Sabine et al.*, 2004].



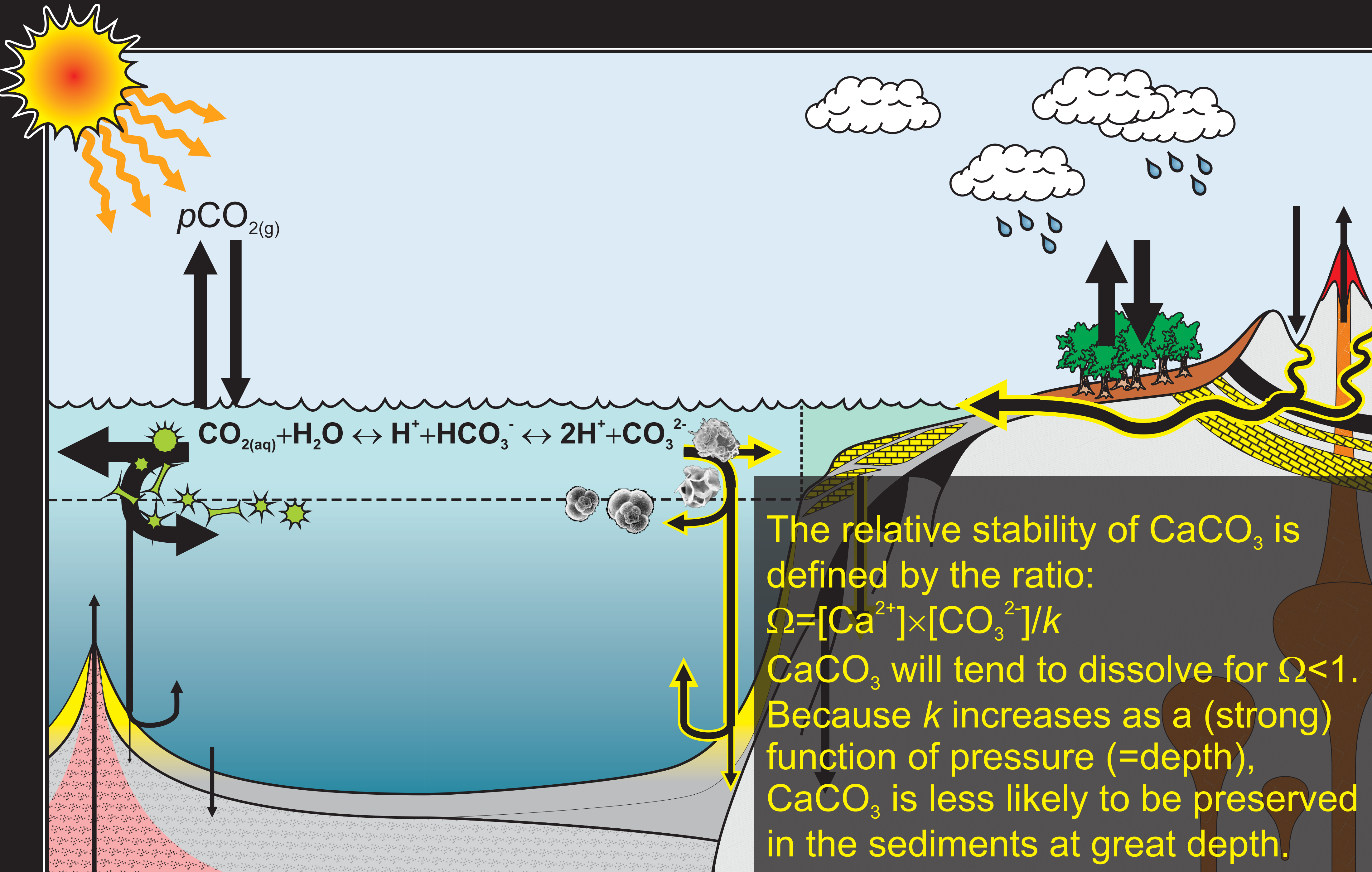
From: *Sabine et al.* [2004] (*Science* 305)


Emissions (PgC yr-1)
~4500 PgC
Atmospheric CO2 (ppm)
Ocean invasion only
34% (645 ppm) remaining
CO2 speciation (mmol kg-1)
year
From: Ridgwell and Hargreaves [2007] (GBC)

The marine carbon cycle - dynamics



The marine carbon cycle - dynamics



The relative stability of $CaCO_3$ is defined by the ratio:

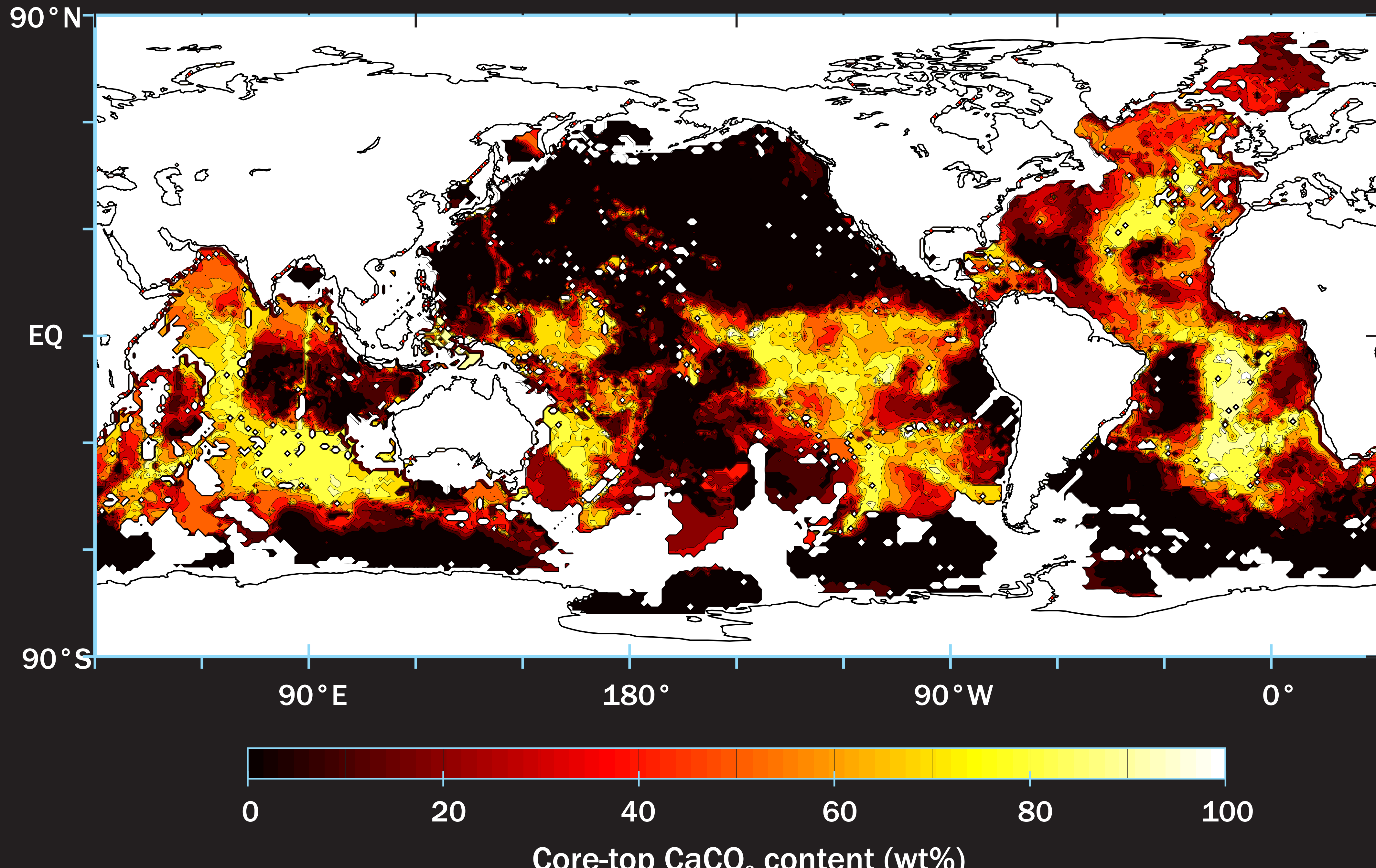
$\Omega=[Ca^{2+}]\times[CO_3^{2-}]/k$

$CaCO_3$ will tend to dissolve for $\Omega<1$.

Because k increases as a (strong) function of pressure (=depth), $CaCO_3$ is less likely to be preserved in the sediments at great depth.

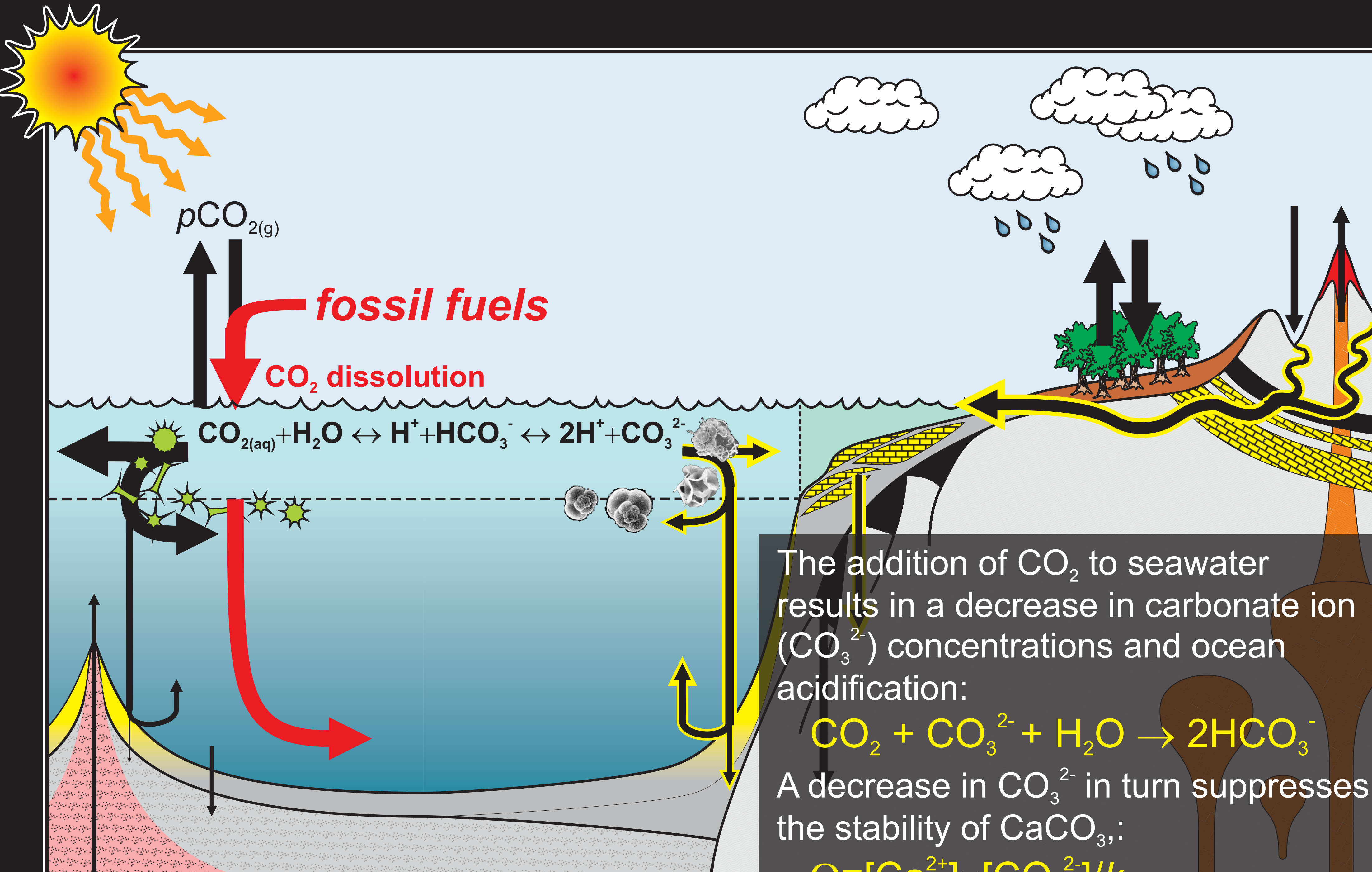
see; *Ridgwell and Zeebe* [2005] (*EPSL* 234) for a review of global carbonate cycling through Earth history

Sediments and global biogeochemical cycles



From: *Archer* [1996] (*GBC*)

The marine carbon cycle - dynamics



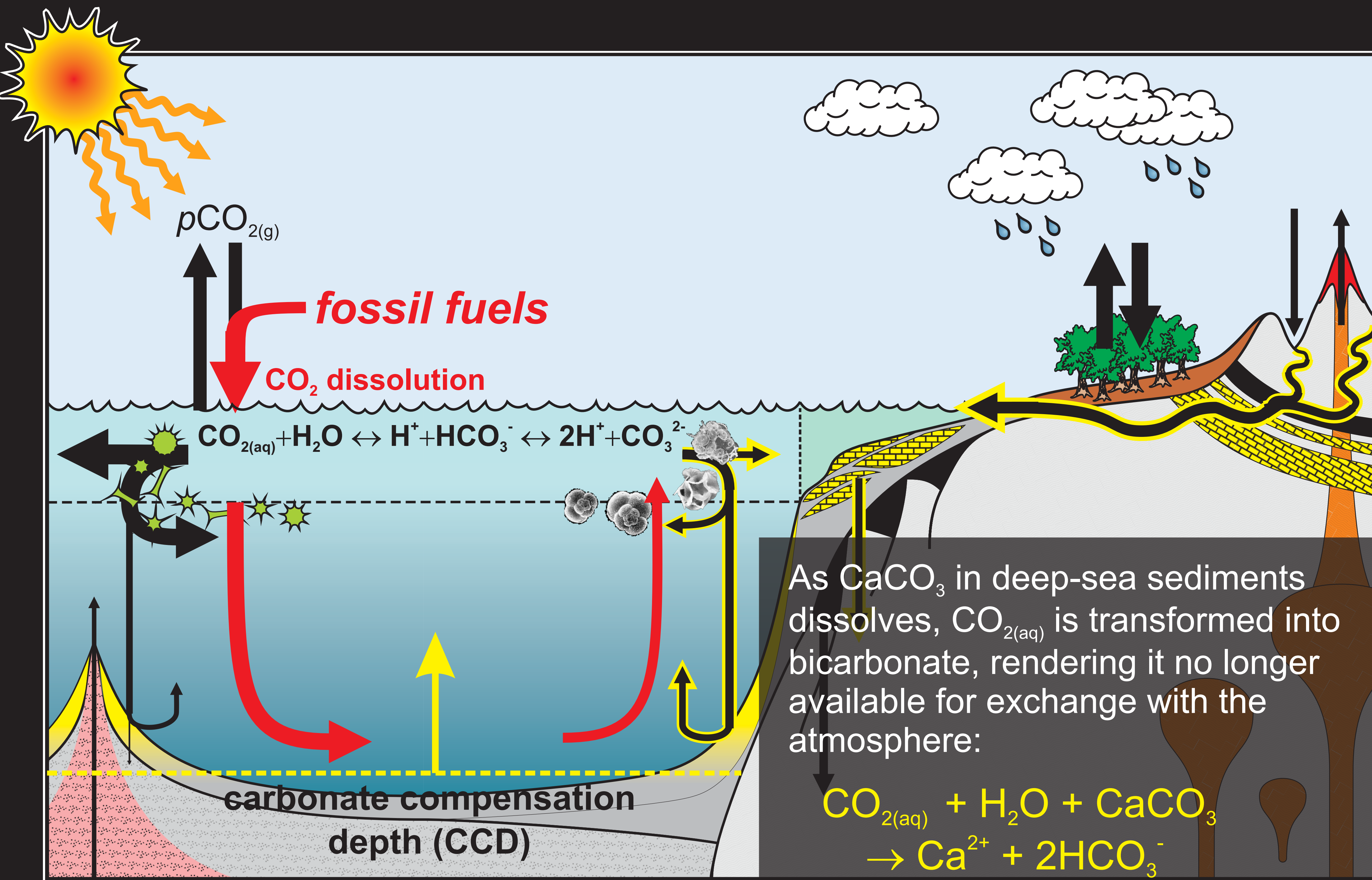
The addition of CO_2 to seawater results in a decrease in carbonate ion (CO_3^{2-}) concentrations and ocean acidification:

$$CO_2 + CO_3^{2-} + H_2O \rightarrow 2HCO_3^-$$

A decrease in CO_3^{2-} in turn suppresses the stability of $CaCO_3$,:

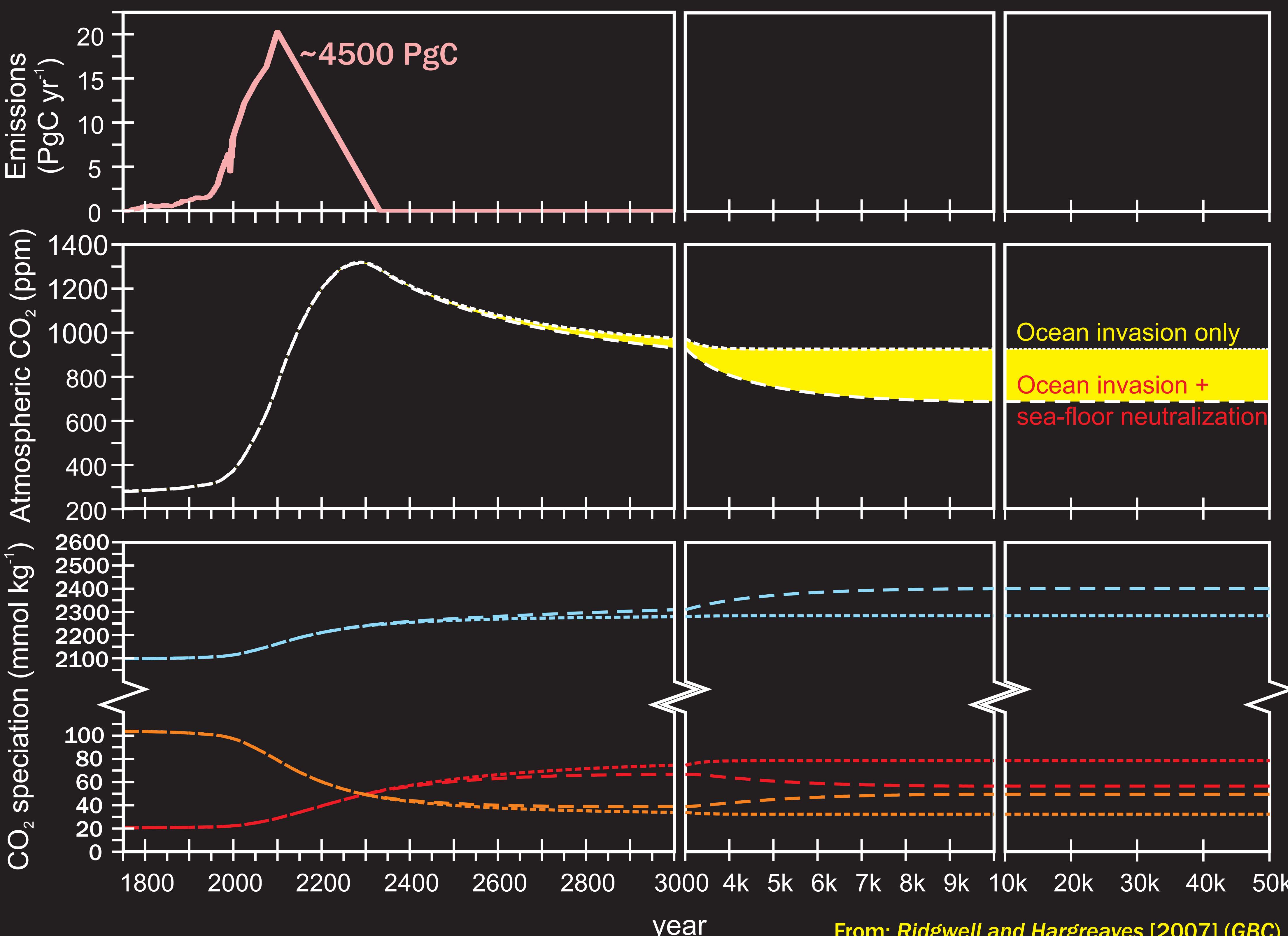
$$\Omega = [Ca^{2+}] \times [CO_3^{2-}]/k$$

The marine carbon cycle - dynamics



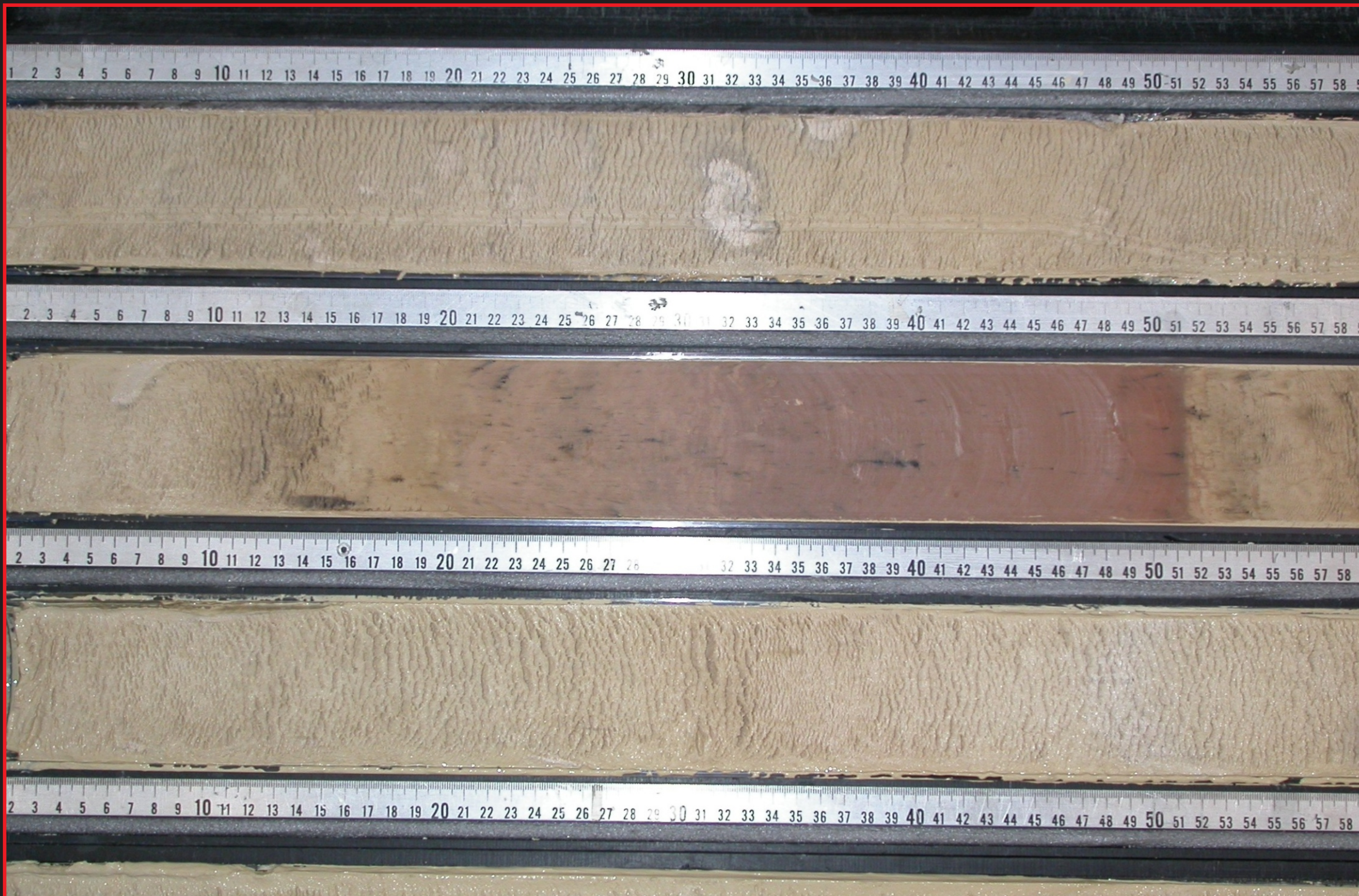
As $CaCO_3$ in deep-sea sediments dissolves, $CO_{2(aq)}$ is transformed into bicarbonate, rendering it no longer available for exchange with the atmosphere:

$$CO_{2(aq)} + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-$$



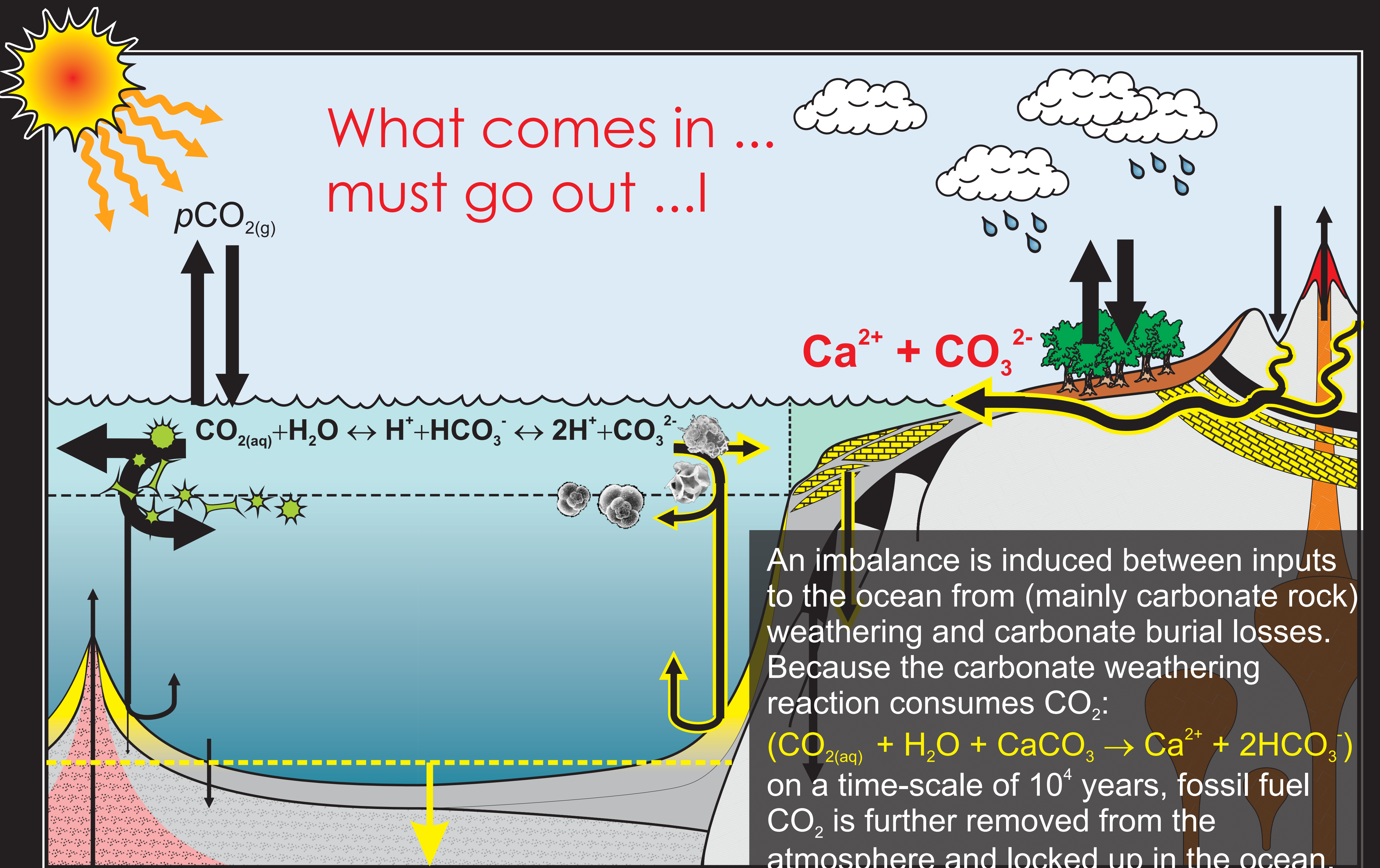
From: *Ridgwell and Hargreaves* [2007] (*GBC*)

The marine carbon cycle - dynamics



Sediments spanning the Palaeocene-Eocene boundary recovered from ODP Leg 208 (Walvis Ridge)
Picture courtesy of Dani Schmidt (University of Bristol)

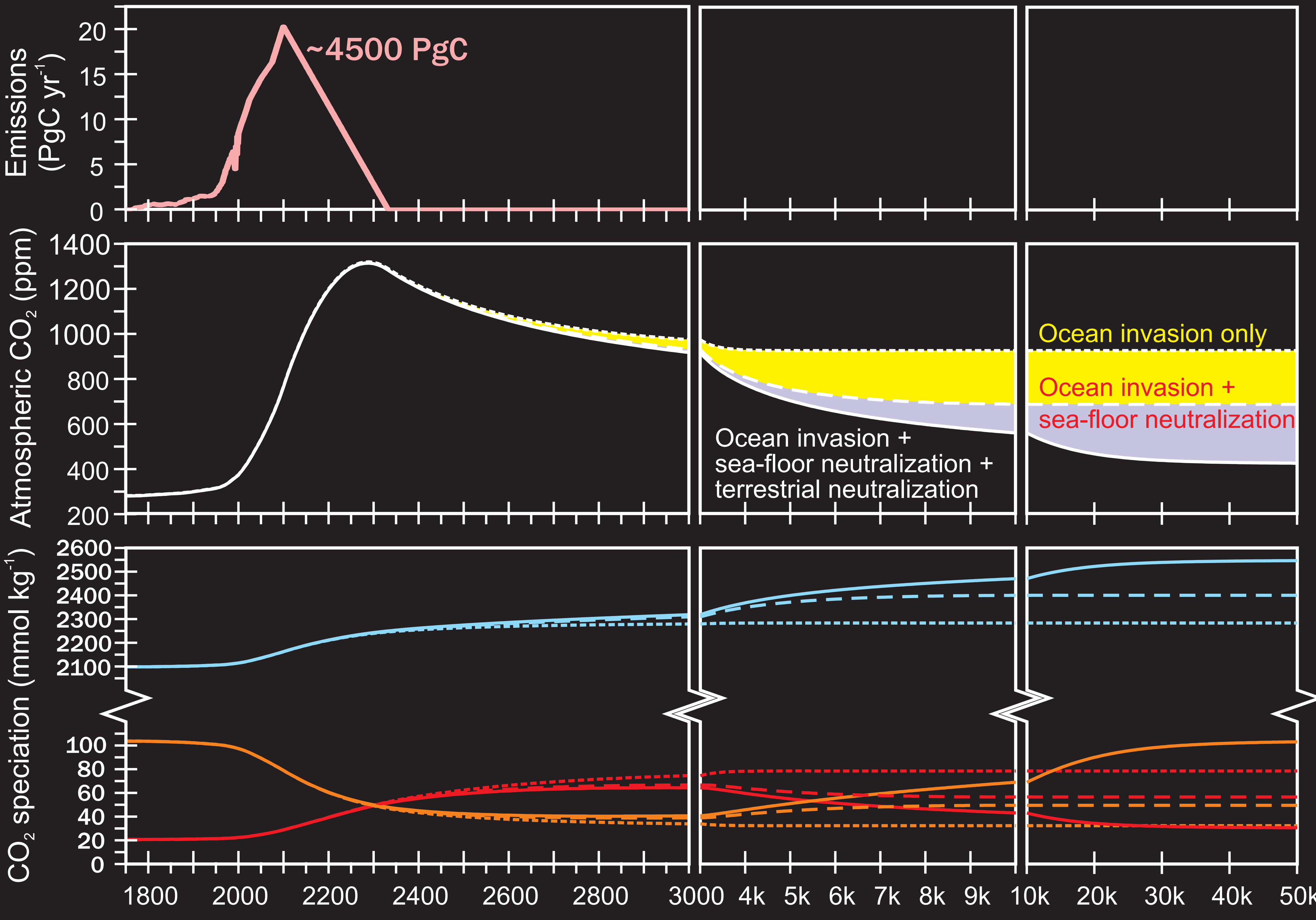
Deep-sea sedimentary buffering



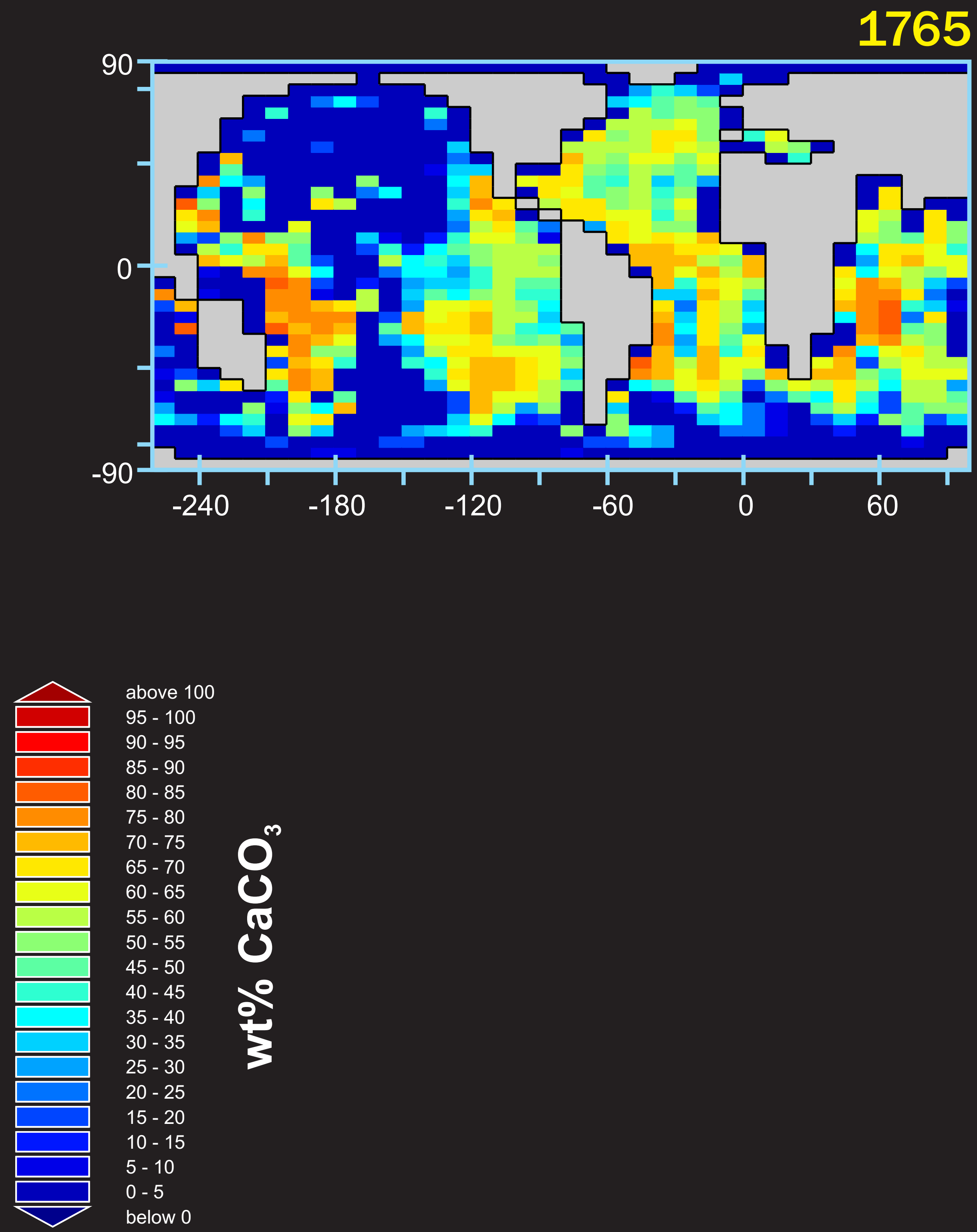
An imbalance is induced between inputs to the ocean from (mainly carbonate rock) weathering and carbonate burial losses. Because the carbonate weathering reaction consumes CO_2:

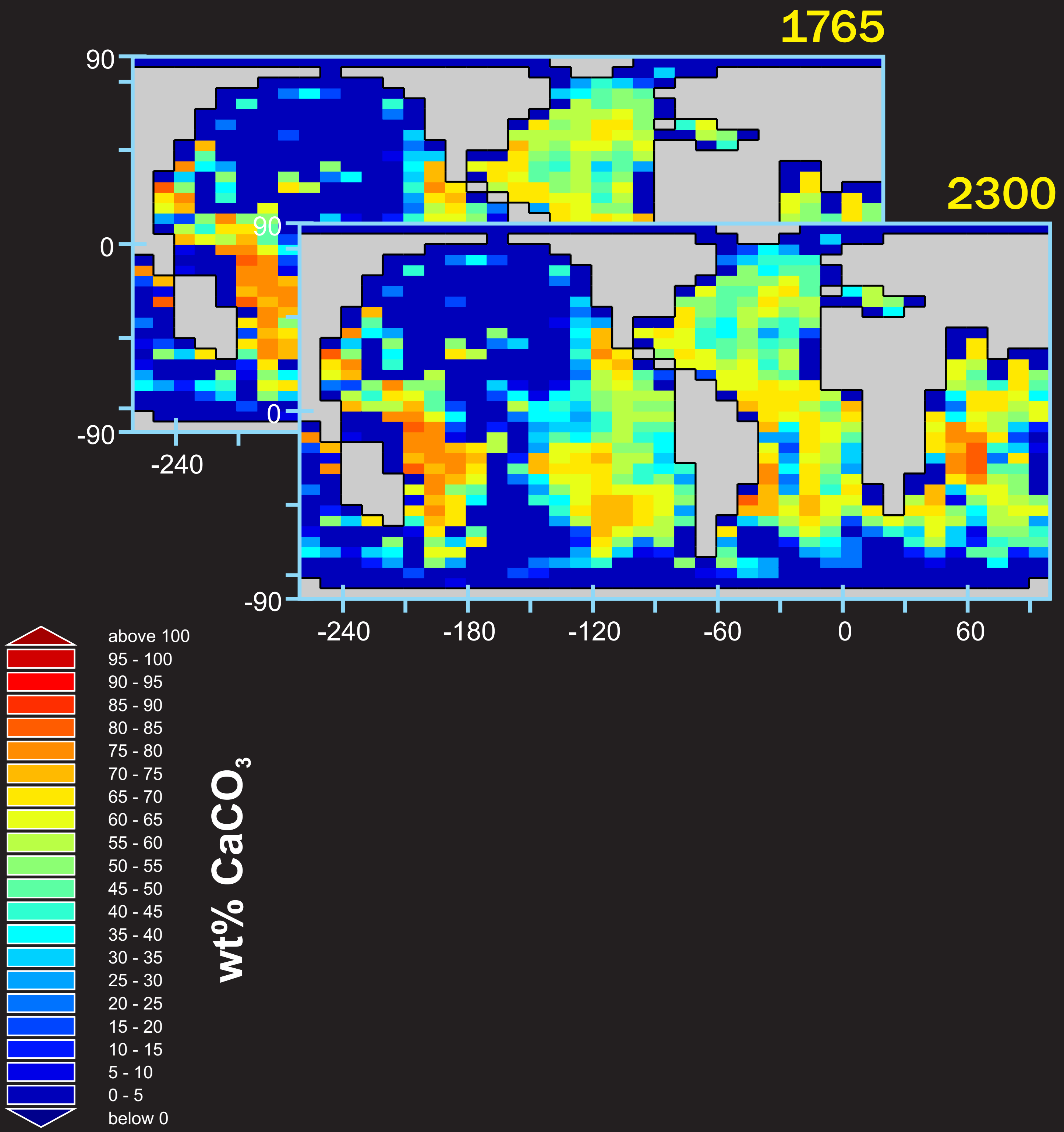
$(CO_{2(aq)} + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-)$

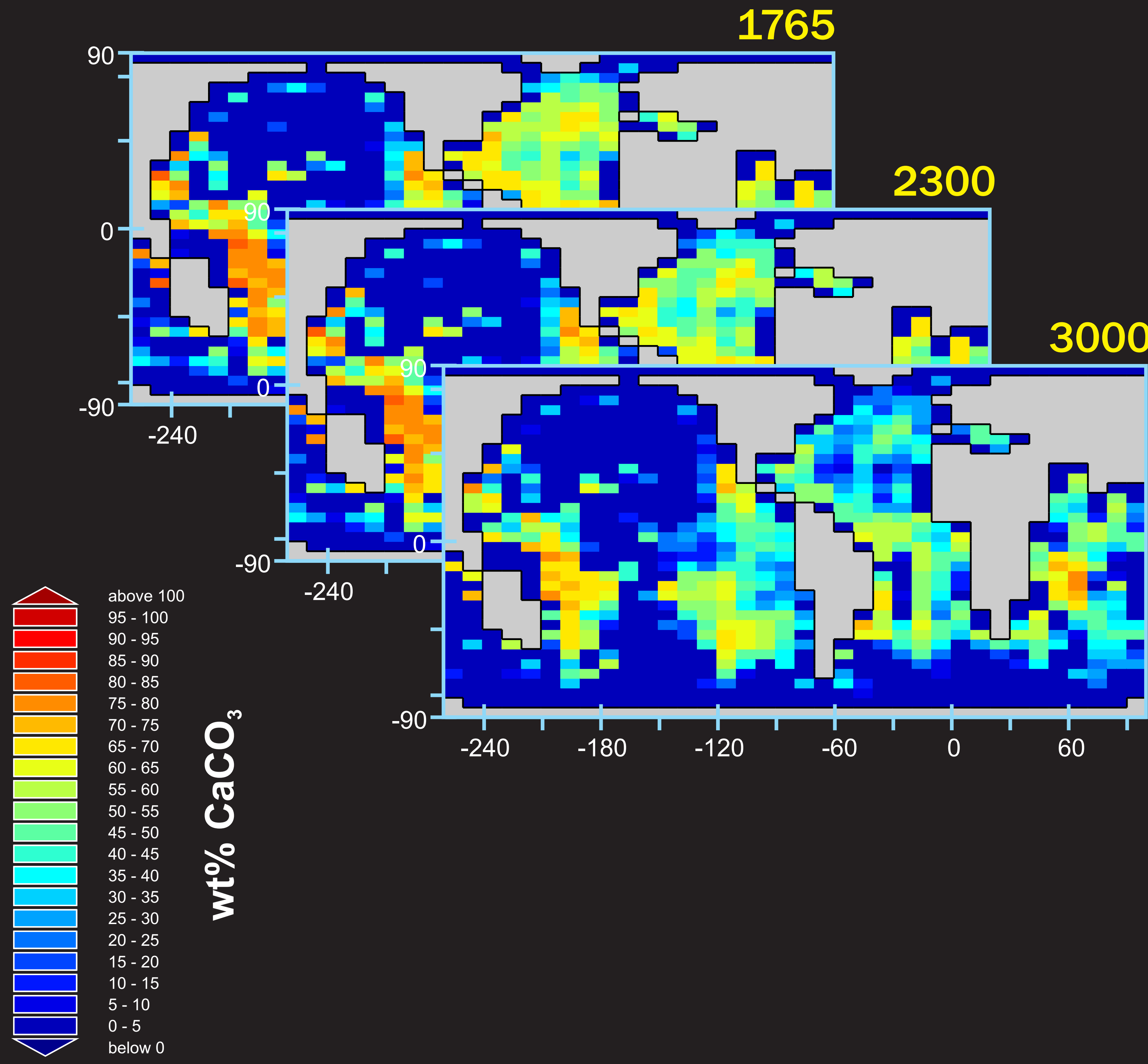
on a time-scale of 10^4 years, fossil fuel CO_2 is further removed from the atmosphere and locked up in the ocean.



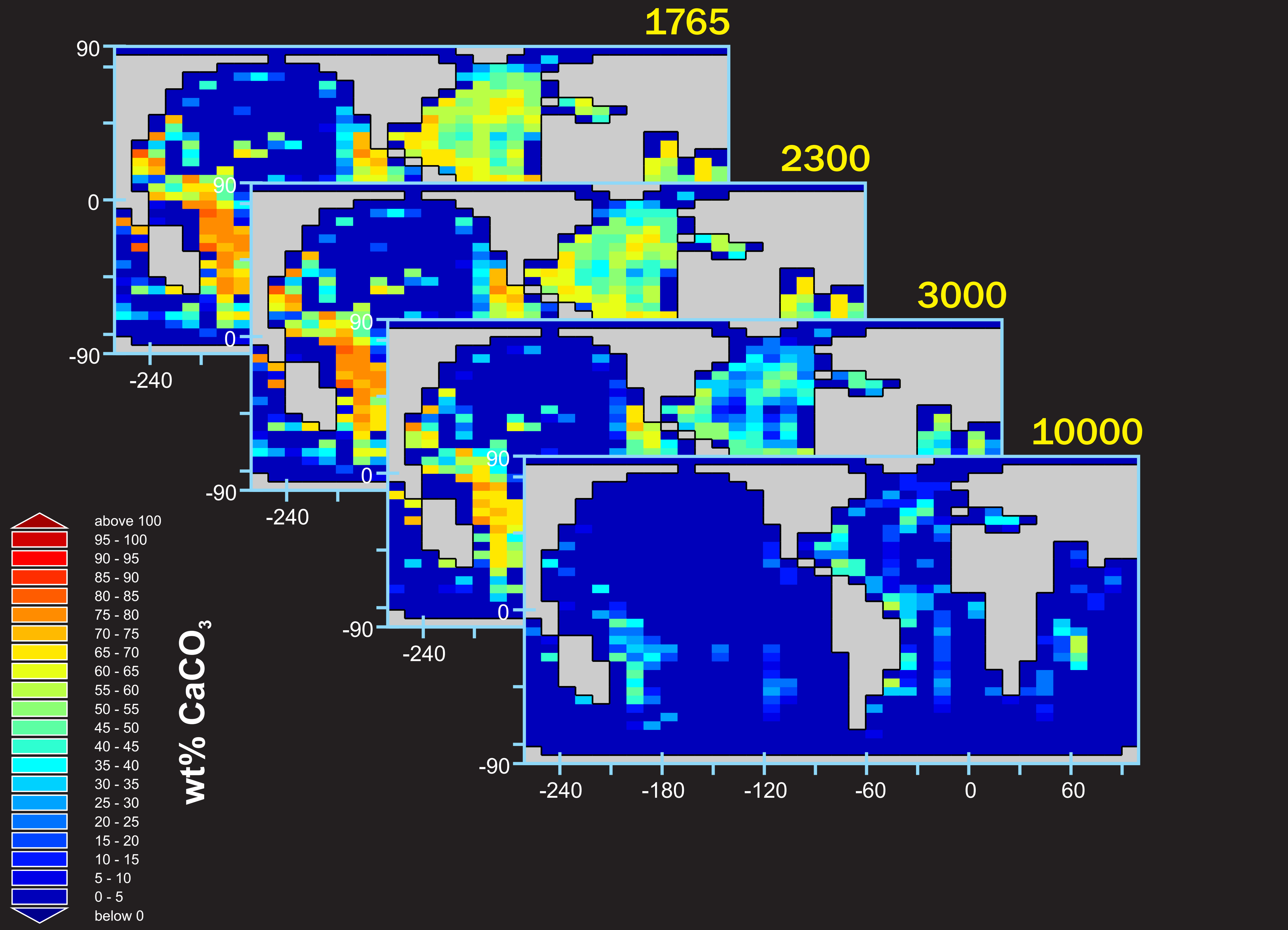
From: *Ridgwell and Hargreaves* [2007] (*GBC*)


1765
90
0
-90
-240
-180
-120
-60
0
60
above 100
95 - 100
90 - 95
85 - 90
80 - 85
75 - 80
70 - 75
65 - 70
60 - 65
55 - 60
50 - 55
45 - 50
40 - 45
35 - 40
30 - 35
25 - 30
20 - 25
15 - 20
10 - 15
5 - 10
0 - 5
below 0
wt% $CaCO_3$

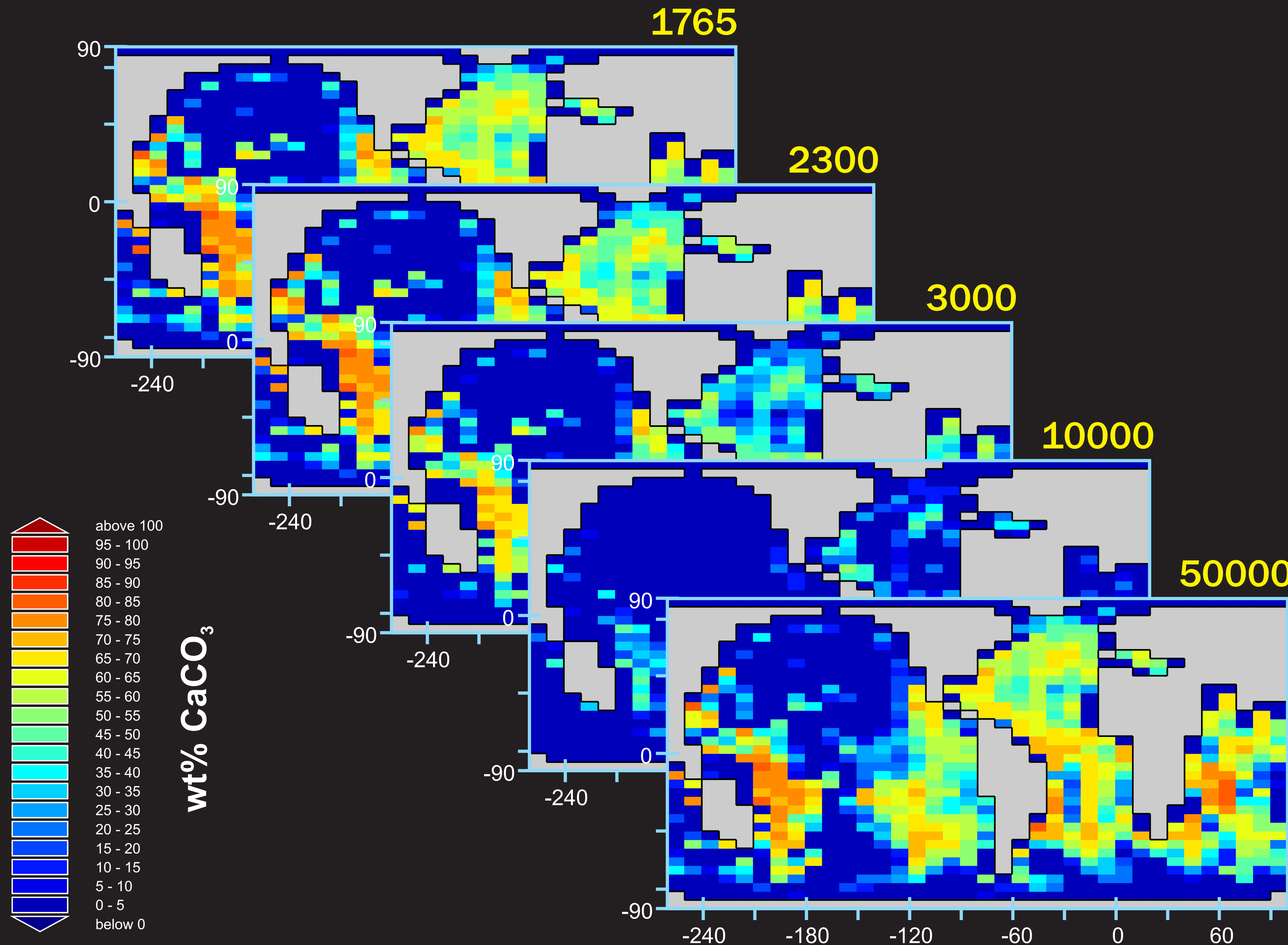

1765
2300
90
0
-90
-240
90
0
-90
-240
-180
-120
-60
0
60
above 100
95 - 100
90 - 95
85 - 90
80 - 85
75 - 80
70 - 75
65 - 70
60 - 65
55 - 60
50 - 55
45 - 50
40 - 45
35 - 40
30 - 35
25 - 30
20 - 25
15 - 20
10 - 15
5 - 10
0 - 5
below 0
wt% $CaCO_3$



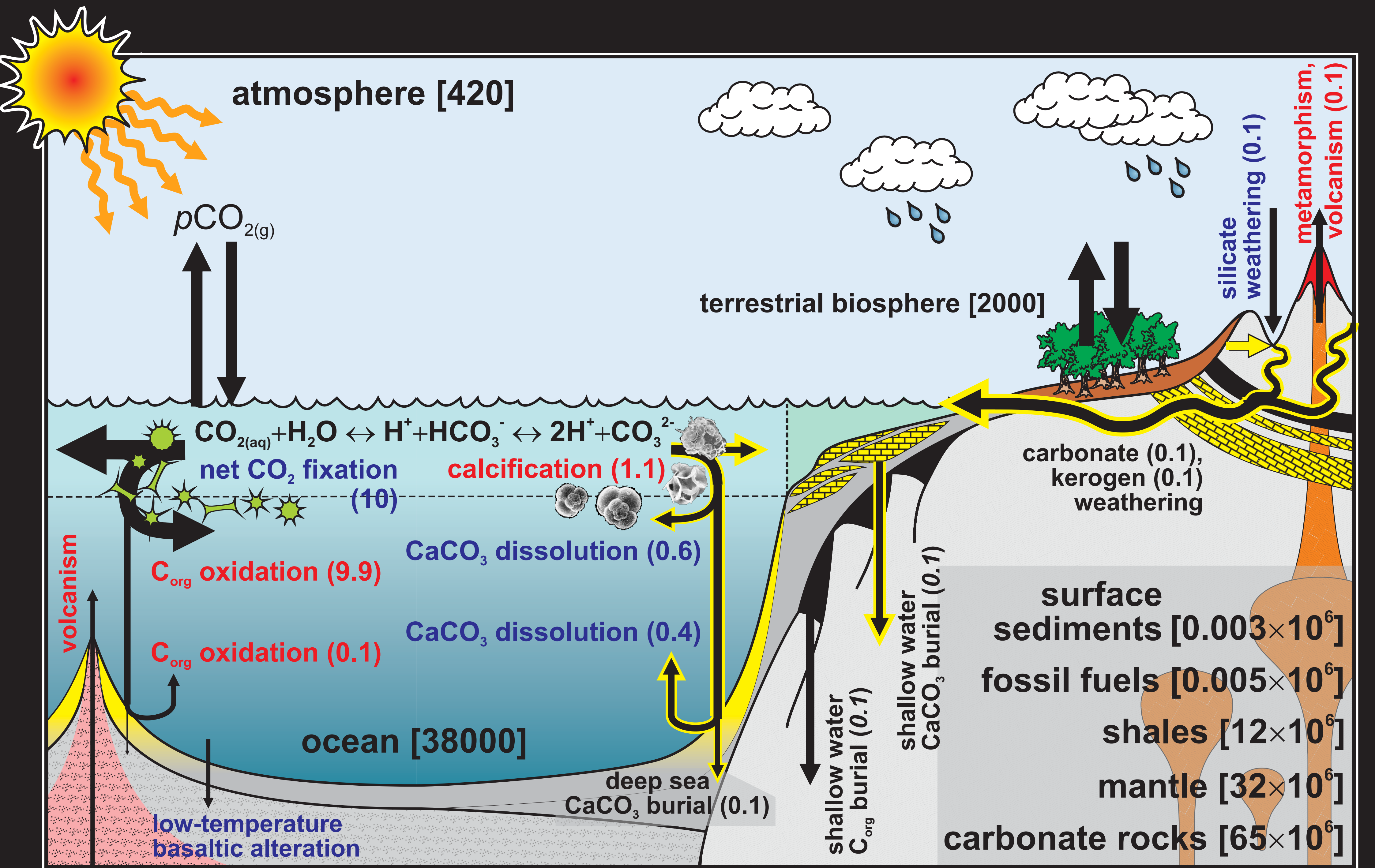
1765
2300
3000
90
0
-90
-240
-180
-120
-60
60
above 100
95 - 100
90 - 95
85 - 90
80 - 85
75 - 80
70 - 75
65 - 70
60 - 65
55 - 60
50 - 55
45 - 50
40 - 45
35 - 40
30 - 35
25 - 30
20 - 25
15 - 20
10 - 15
5 - 10
0 - 5
below 0
wt% $CaCO_3$



1765
2300
3000
10000
90
0
-90
-240
-180
-120
-60
0
60
above 100
95 - 100
90 - 95
85 - 90
80 - 85
75 - 80
70 - 75
65 - 70
60 - 65
55 - 60
50 - 55
45 - 50
40 - 45
35 - 40
30 - 35
25 - 30
20 - 25
15 - 20
10 - 15
5 - 10
0 - 5
below 0
wt% $CaCO_3$


1765
2300
3000
10000
50000
90
0
-90
-240
-180
-120
-60
0
60
above 100
95 - 100
90 - 95
85 - 90
80 - 85
75 - 80
70 - 75
65 - 70
60 - 65
55 - 60
50 - 55
45 - 50
40 - 45
35 - 40
30 - 35
25 - 30
20 - 25
15 - 20
10 - 15
5 - 10
0 - 5
below 0
wt% $CaCO_3$

The marine carbon cycle - dynamics



The marine carbon cycle - dynamics

Terrestrial weathering can be (approximately equally) divided into carbonate ($CaCO_3$) and calcium-silicate ('$CaSiO_3$') weathering:

(1) $2CO_{2(aq)} + H_2O + CaSiO_3 \rightarrow Ca^{2+} + 2HCO_3^- + SiO_2$

(2) $CO_{2(aq)} + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-$

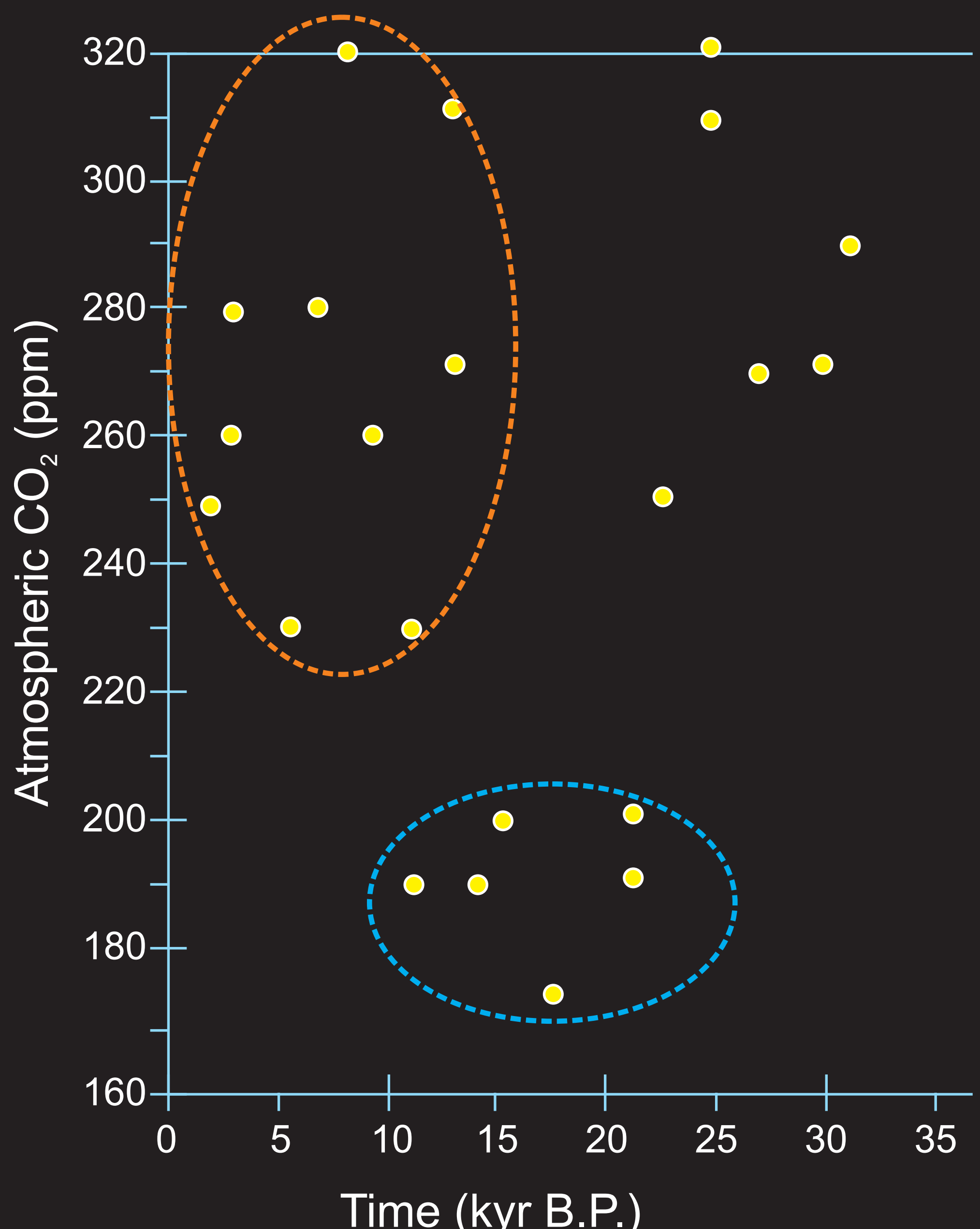
Ultimately, the (alkalinity: Ca^{2+}) weathering products must be removed through carbonate precipitation and burial in marine sediments:

(3) $Ca^{2+} + 2HCO_3^- \rightarrow CO_{2(aq)} + H_2O + CaCO_3$

It can be seen that in (2) + (3), that the CO_2 removed (from the atmosphere) during weathering, is returned upon carbonate precipitation (and burial). In (1) + (3) (silicate weathering) CO_2 is permanently removed to the geological reservoir. This CO_2 must be balanced by mantle (/volcanic) out-gassing on the very long term.

Silicate weathering is a ca. 100 kyr process. Hence, anthropogenic carbon 'pollution' and climate perturbation will persist for hundreds of thousands of years ...

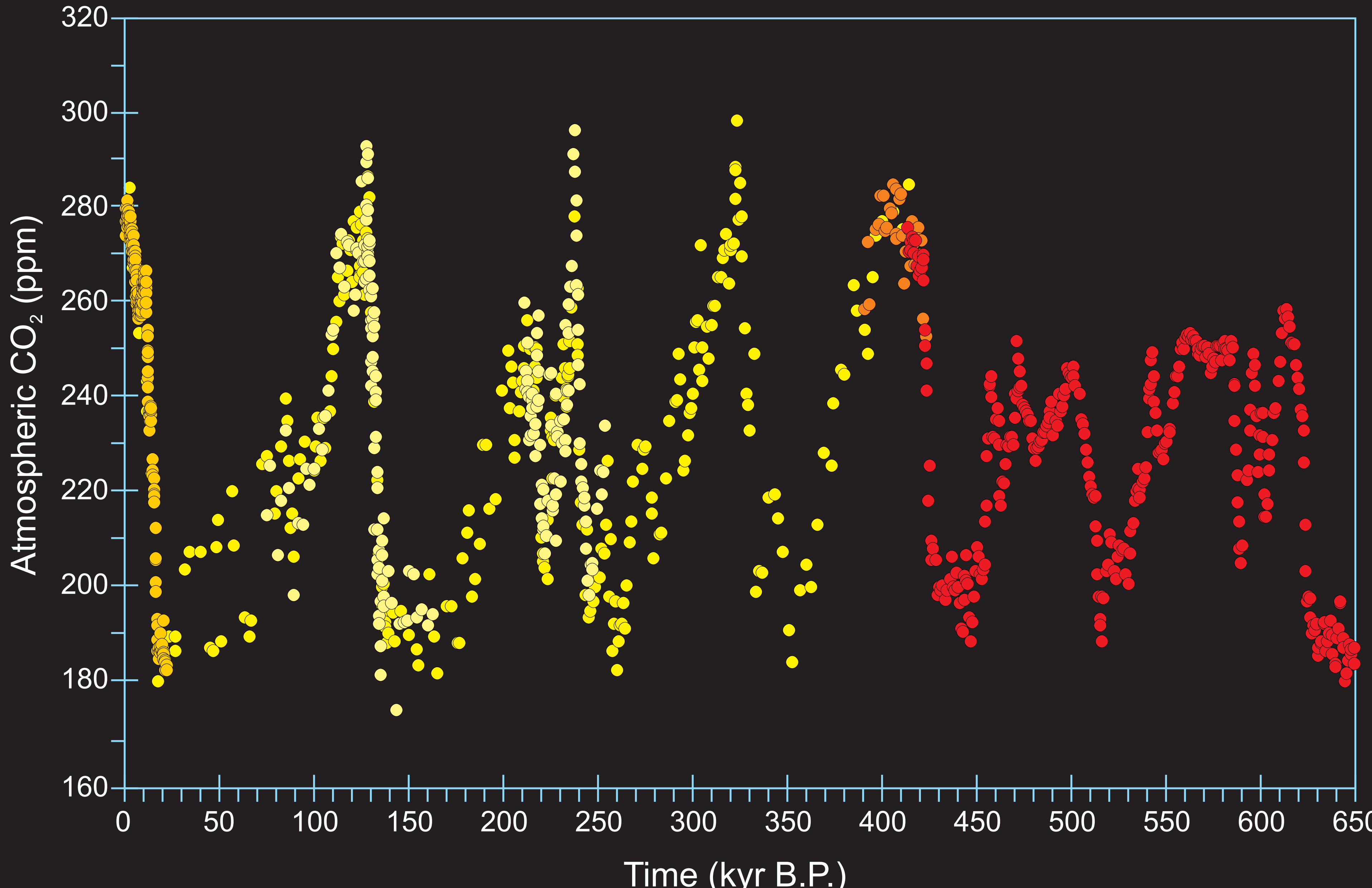
The curious case of glacial CO_2 that was low



Extraction carried out by crushing (rather than melting) ice under vacuum eliminated previous contamination problems. This gave the first reliable evidence for a substantially (ca. 50%) lower glacial CO_2 concentration compared to the modern

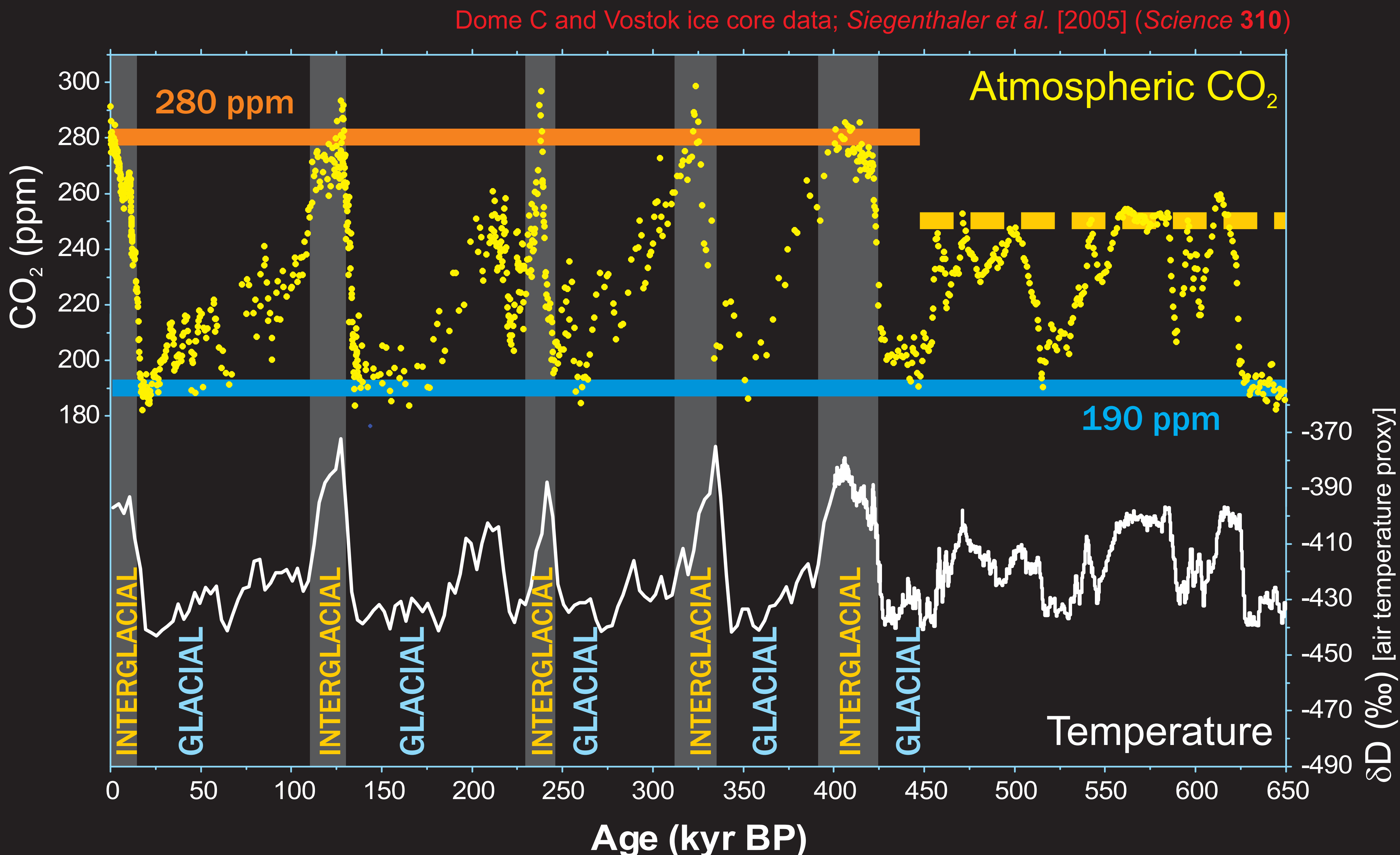
Dome C ice core; Delmas et al. [1980] (Nature 284)

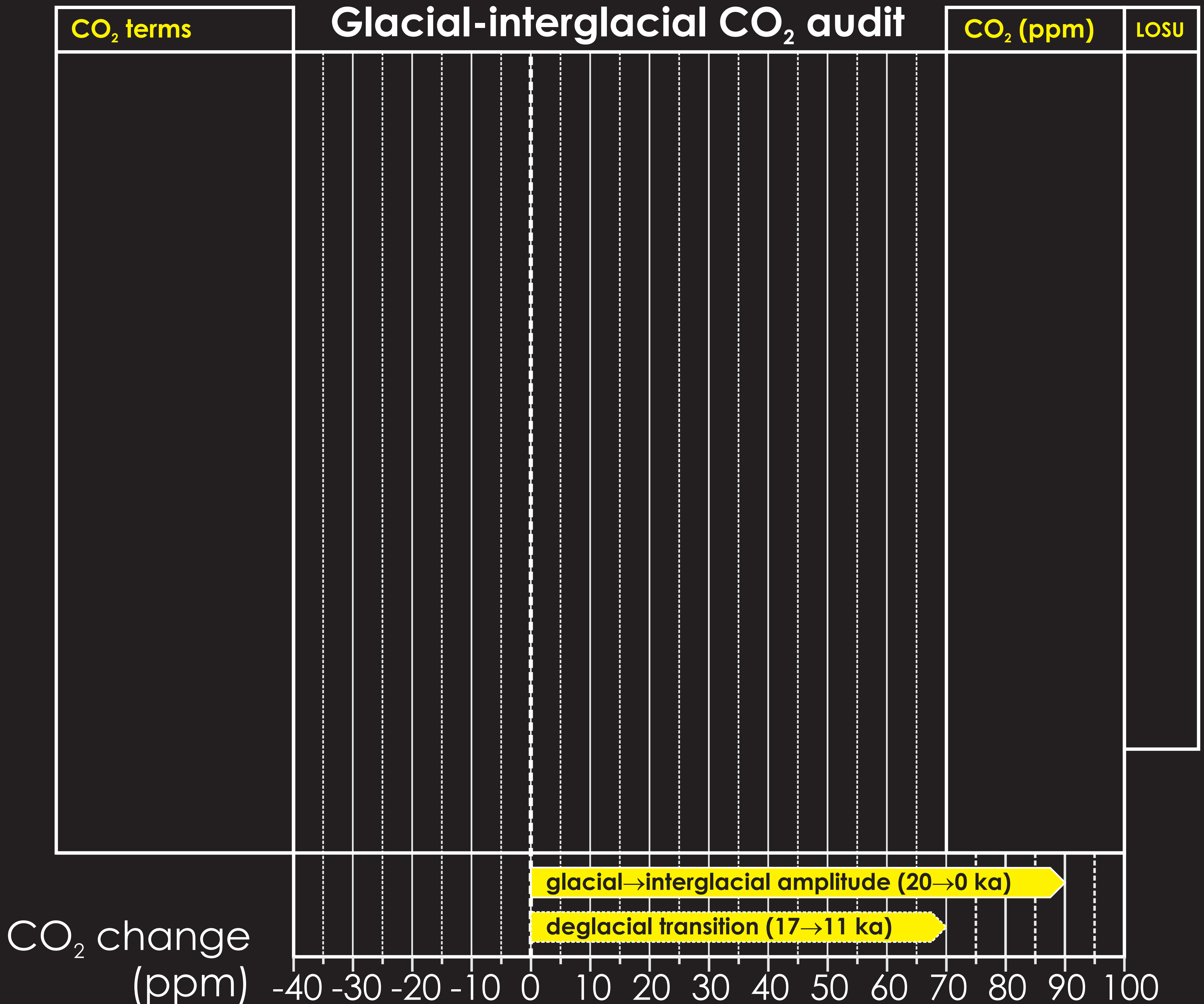
The curious case of glacial CO_2 that was low



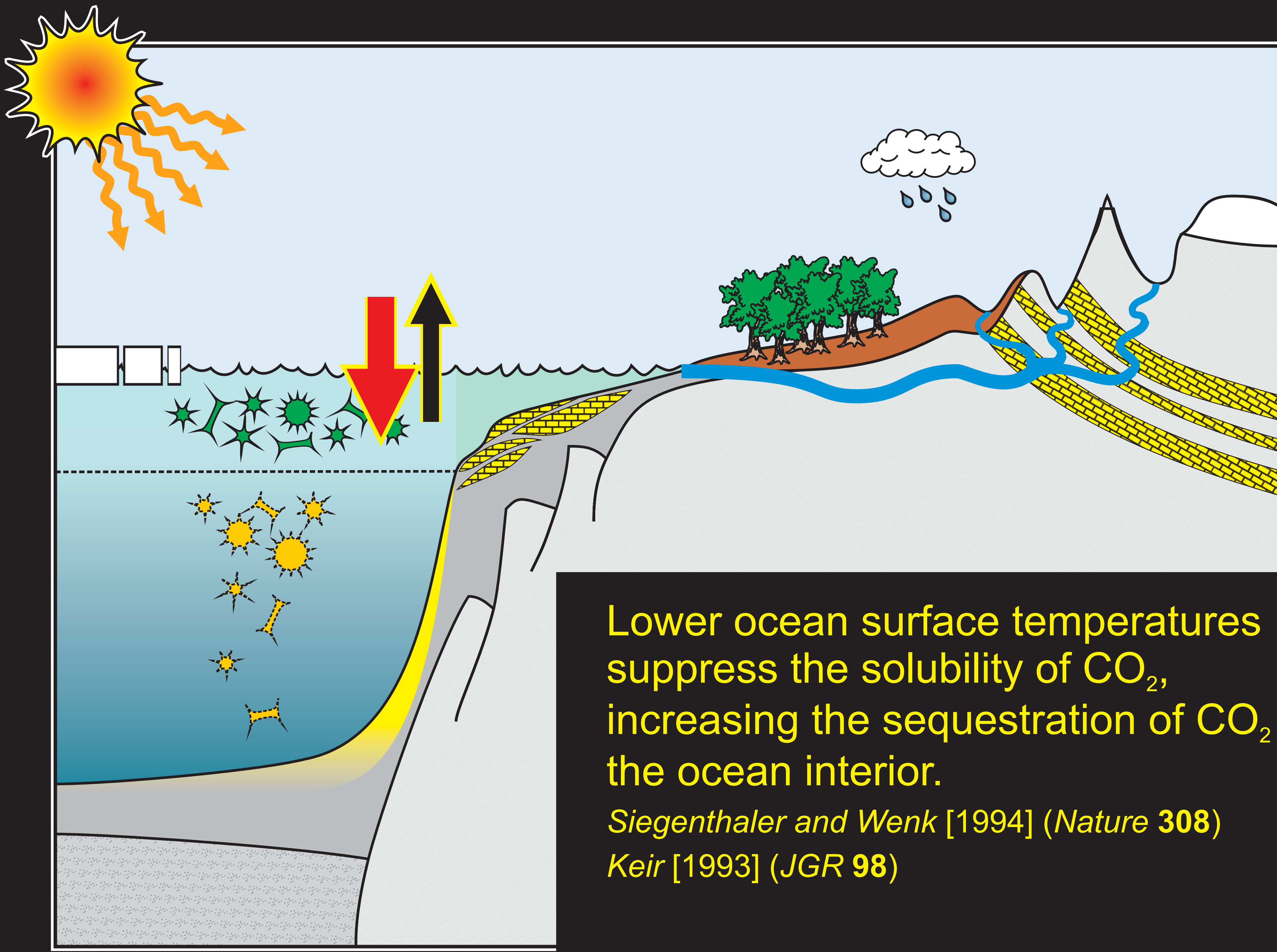
Combined Dome C and Vostok ice core data

The curious case of glacial CO_2 that was low





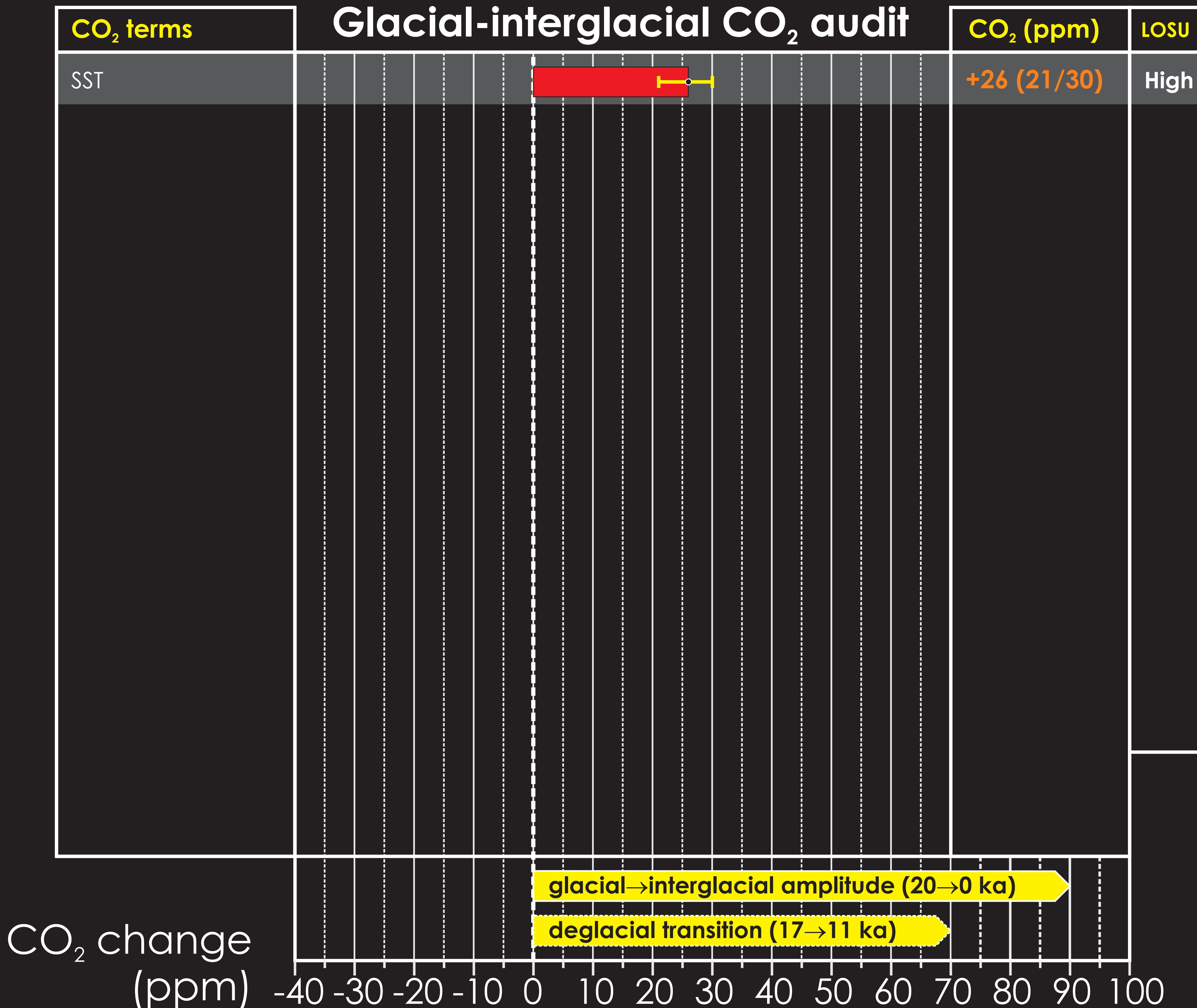
CO2 terms
Glacial-interglacial CO2 audit
CO2 (ppm)
LOSU
glacial→interglacial amplitude (20→0 ka)
deglacial transition (17→11 ka)
CO2 change (ppm)
-40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90 100



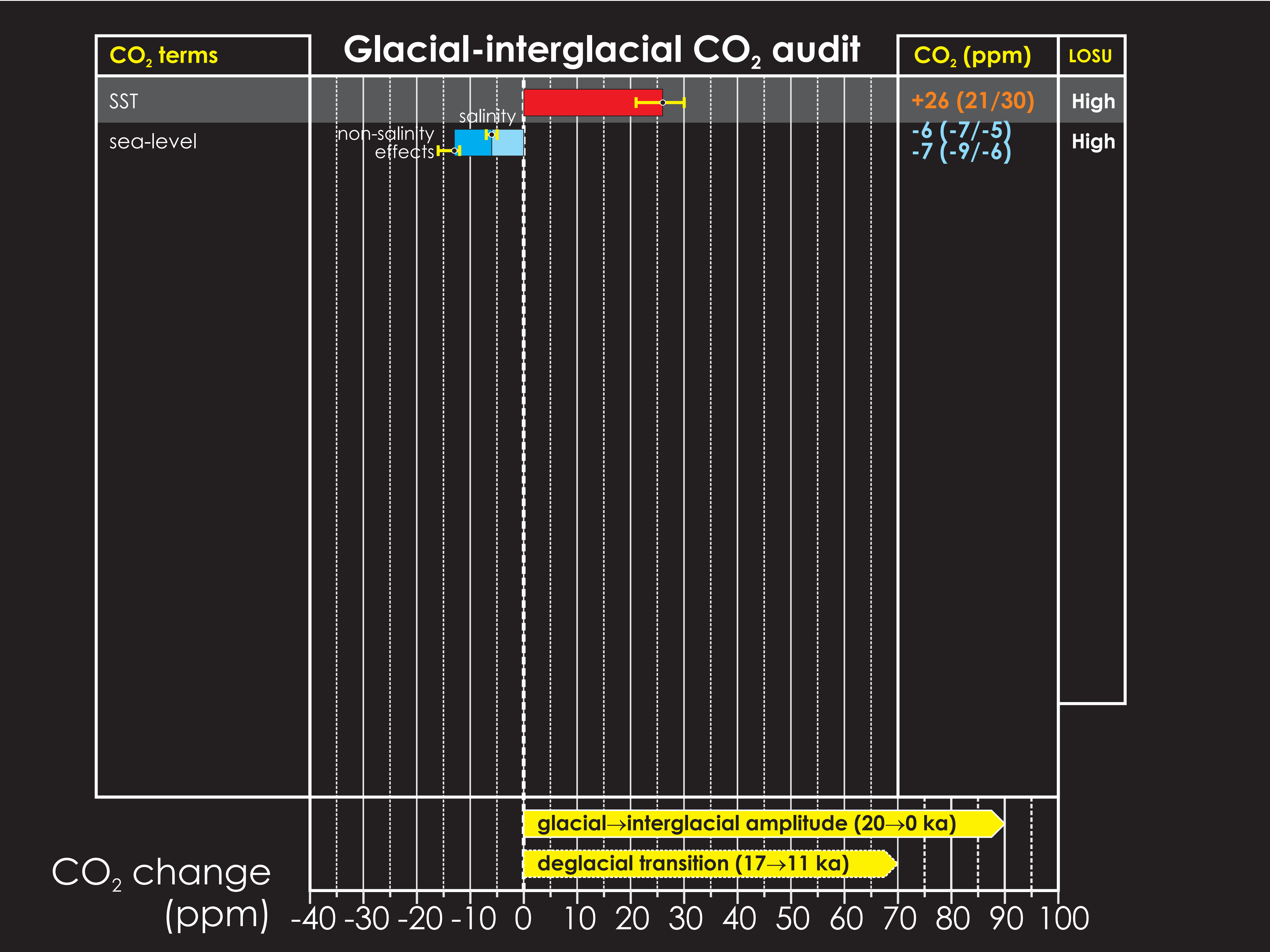
Lower ocean surface temperatures suppress the solubility of CO_2, increasing the sequestration of CO_2 in the ocean interior.

Siegenthaler and Wenk [1994] (*Nature* **308**)

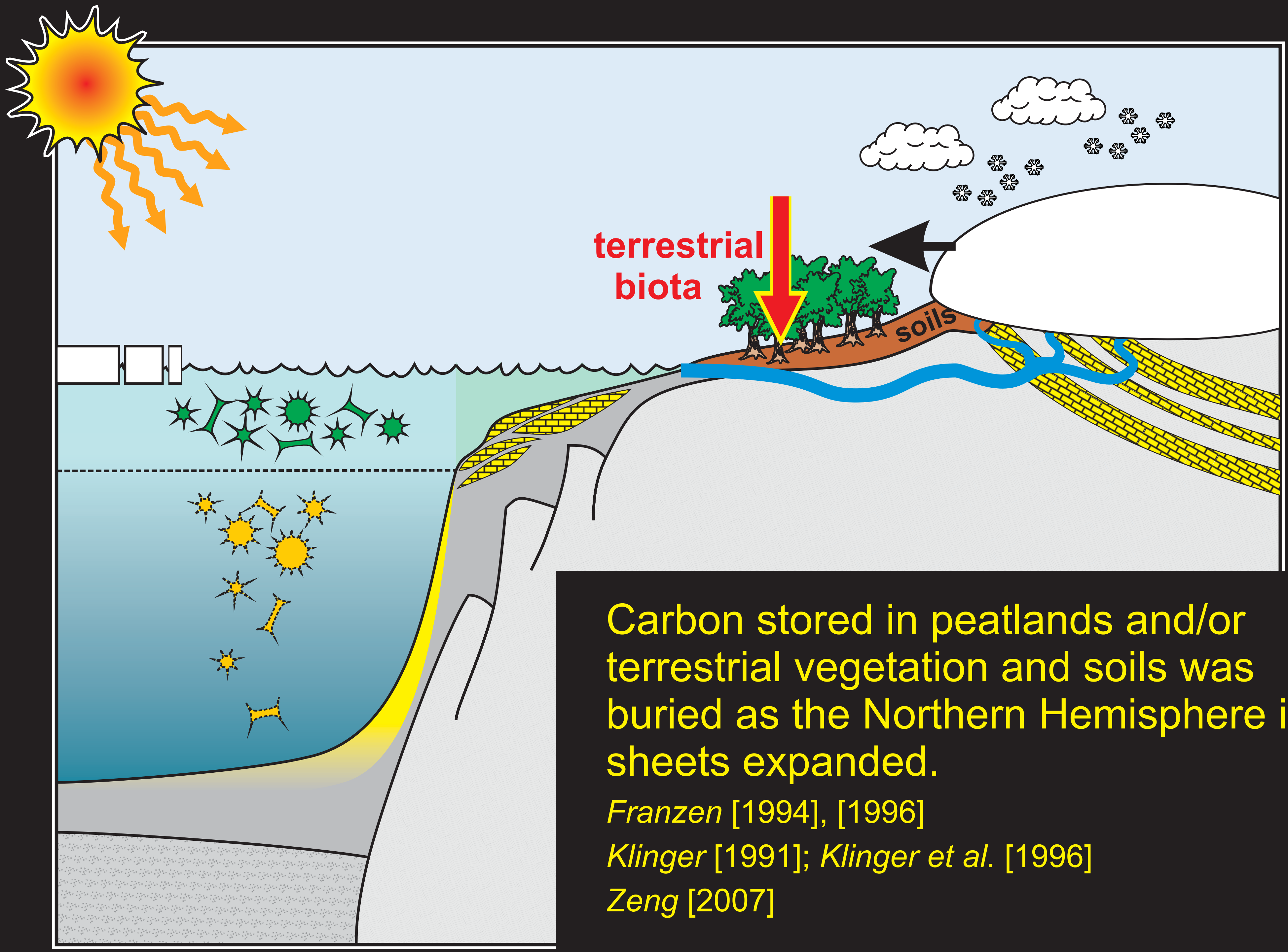
Keir [1993] (*JGR* **98**)



Glacial-interglacial CO_2 audit
CO_2 terms
CO_2 (ppm)
LOSU
SST
+26 (21/30)
High
glacial→interglacial amplitude (20→0 ka)
deglacial transition (17→11 ka)
CO_2 change (ppm)
-40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90 100



Glacial-interglacial CO2 audit
CO2 terms
CO2 (ppm)
LOSU
SST
+26 (21/30)
High
sea-level
salinity
non-salinity
effects
-6 (-7/-5)
-7 (-9/-6)
High
glacial→interglacial amplitude (20→0 ka)
deglacial transition (17→11 ka)
CO2 change
(ppm)
-40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90 100

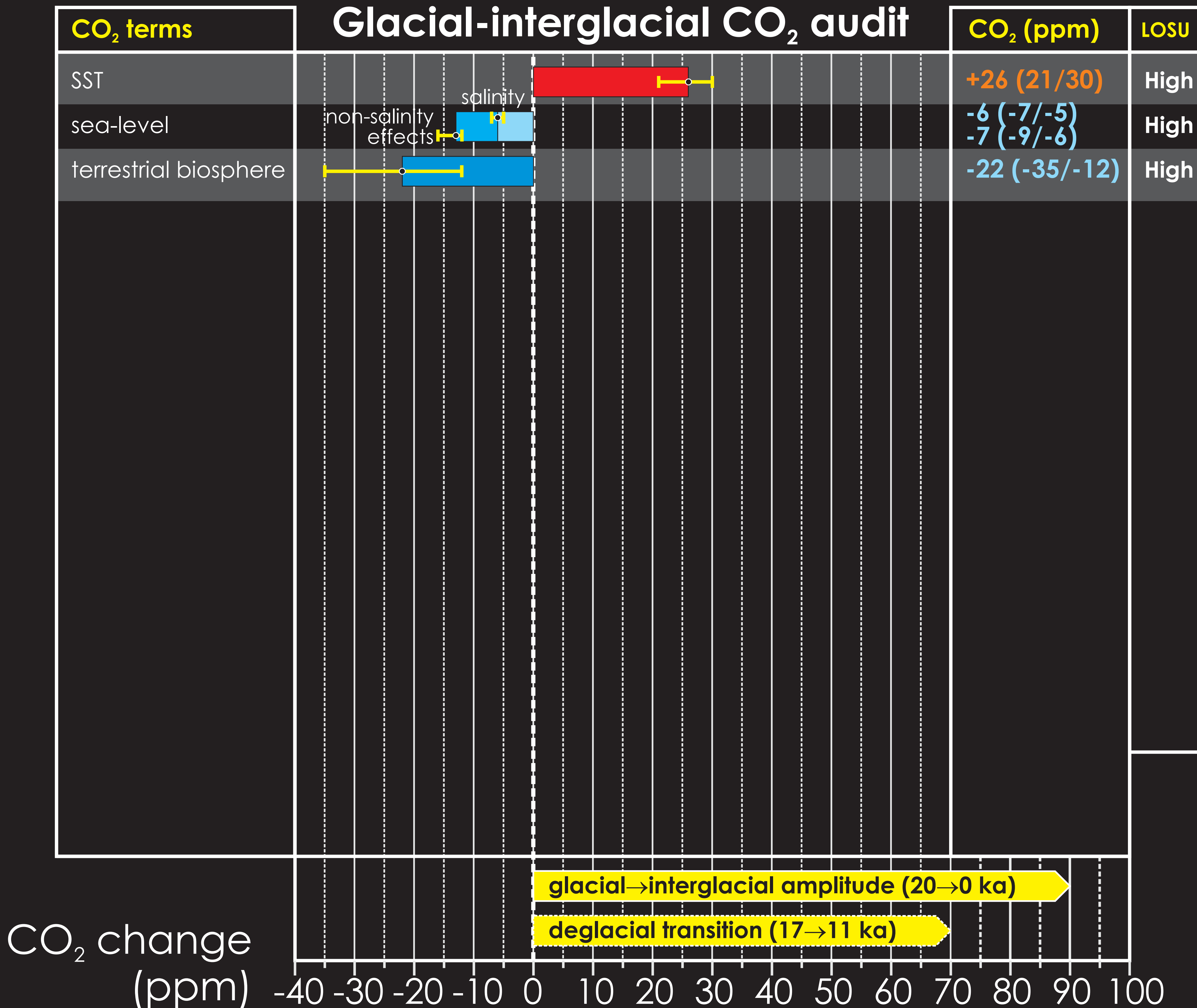


Carbon stored in peatlands and/or terrestrial vegetation and soils was buried as the Northern Hemisphere ice sheets expanded.

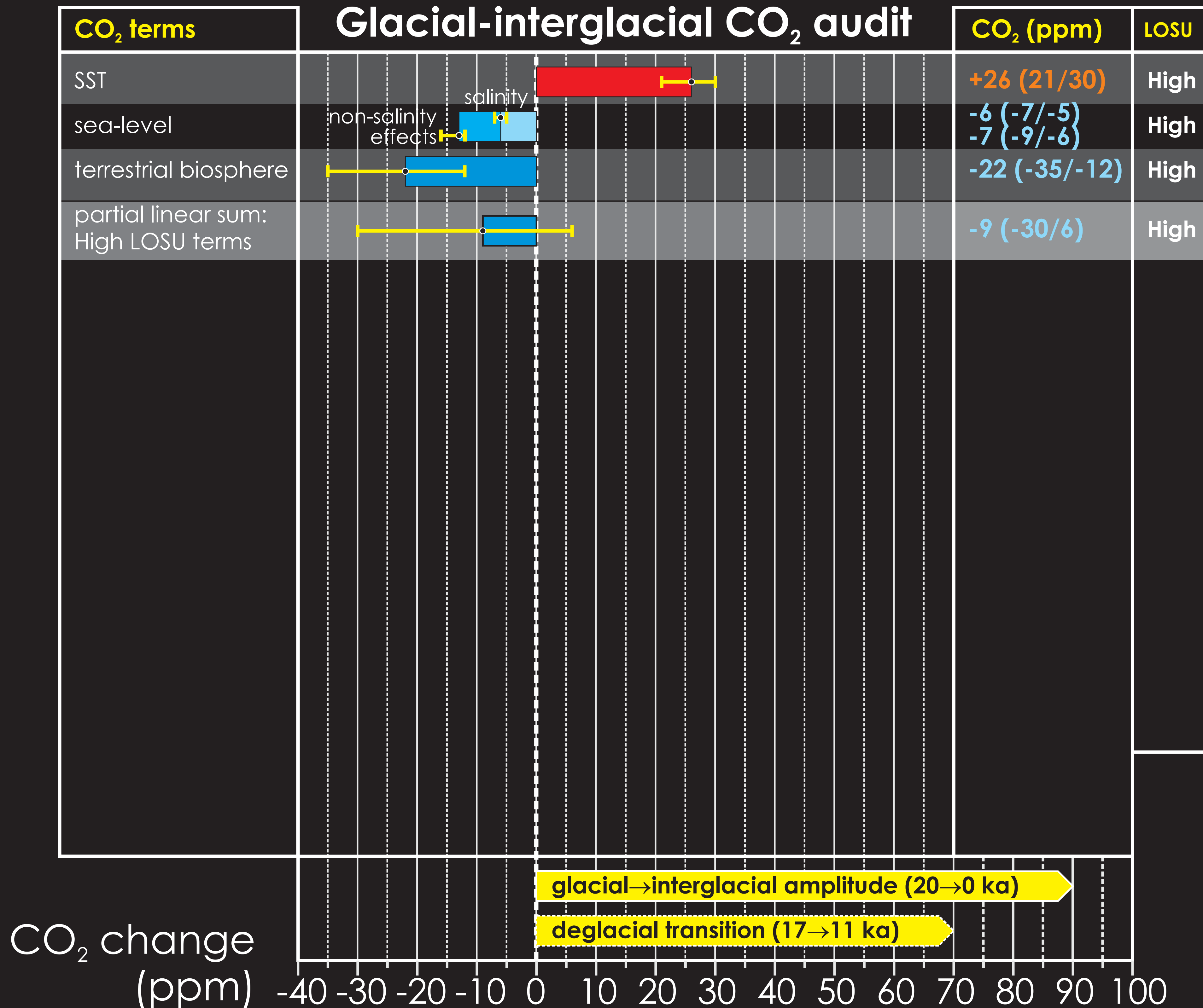
Franzen [1994], [1996]

Klinger [1991]; *Klinger et al.* [1996]

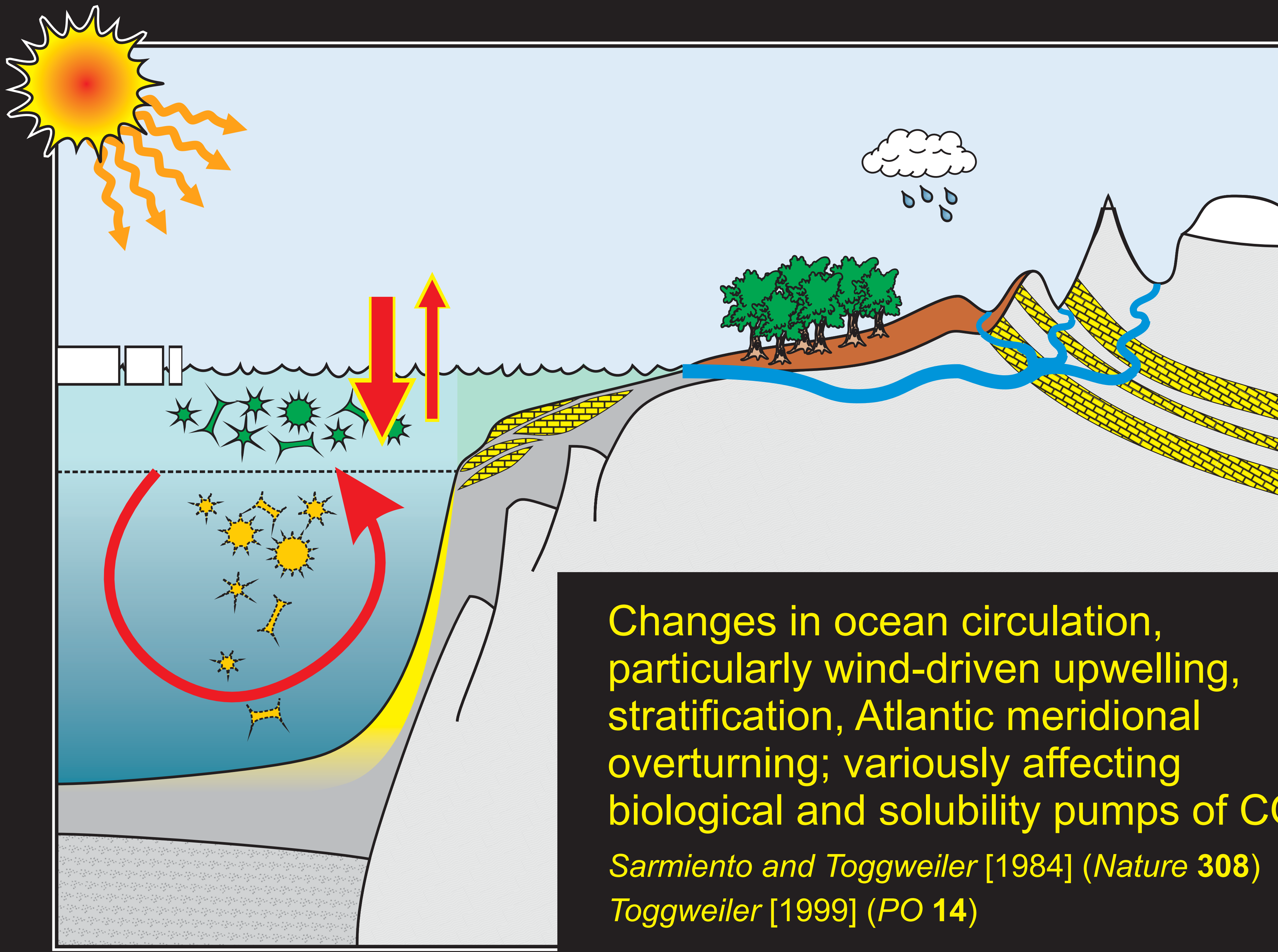
Zeng [2007]



Glacial-interglacial CO2 audit
CO2 terms
CO2 (ppm)
LOSU
SST
+26 (21/30)
High
sea-level
salinity
non-salinity effects
-6 (-7/-5)
-7 (-9/-6)
High
terrestrial biosphere
-22 (-35/-12)
High
glacial→interglacial amplitude (20→0 ka)
deglacial transition (17→11 ka)
CO2 change (ppm)
-40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90 100



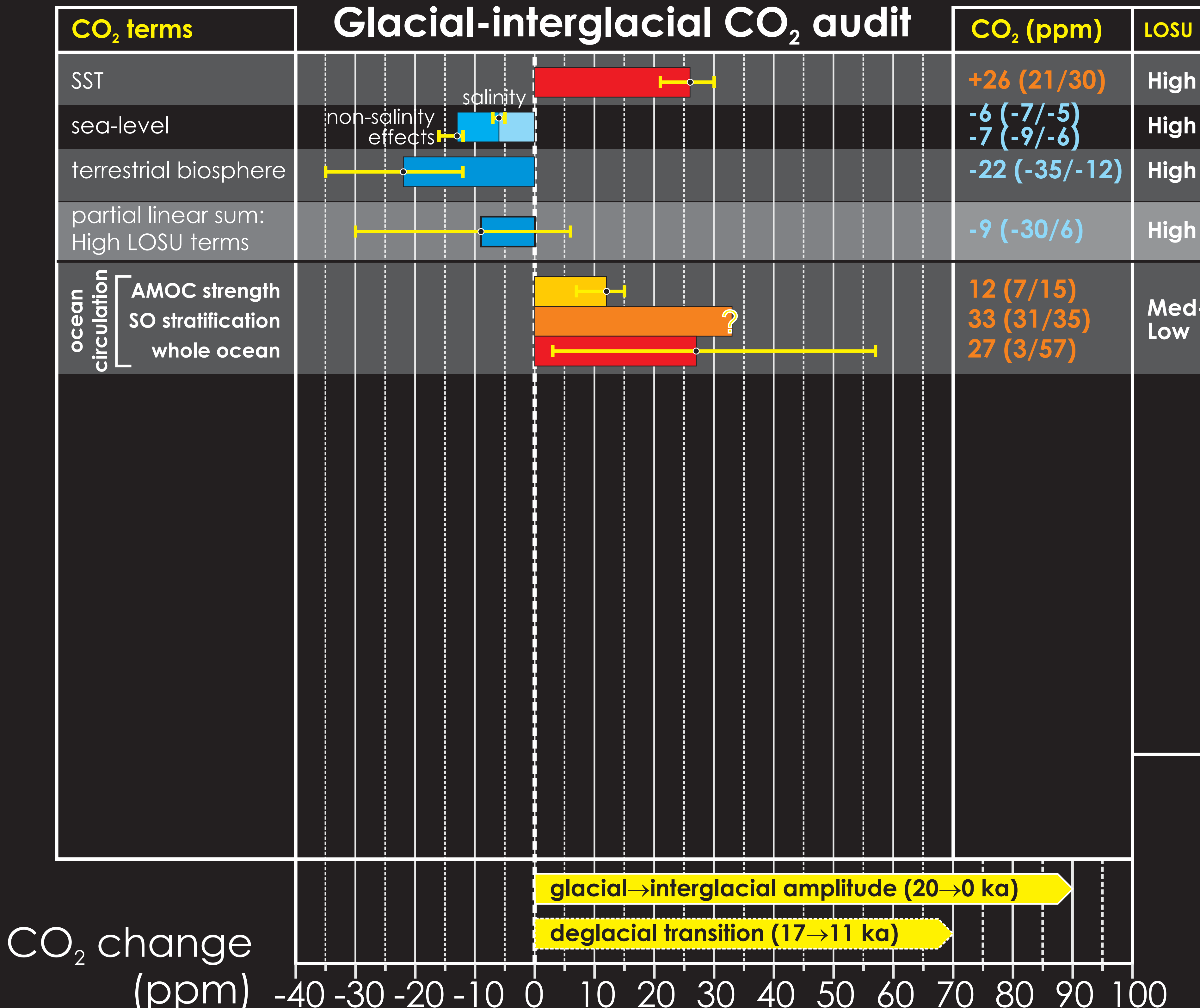
Glacial-interglacial CO2 audit
CO2 terms
CO2 (ppm)
LOSU
SST
+26 (21/30)
High
sea-level
salinity
non-salinity
effects
-6 (-7/-5)
-7 (-9/-6)
High
terrestrial biosphere
-22 (-35/-12)
High
partial linear sum:
High LOSU terms
-9 (-30/6)
High
glacial→interglacial amplitude (20→0 ka)
deglacial transition (17→11 ka)
CO2 change
(ppm)
-40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90 100



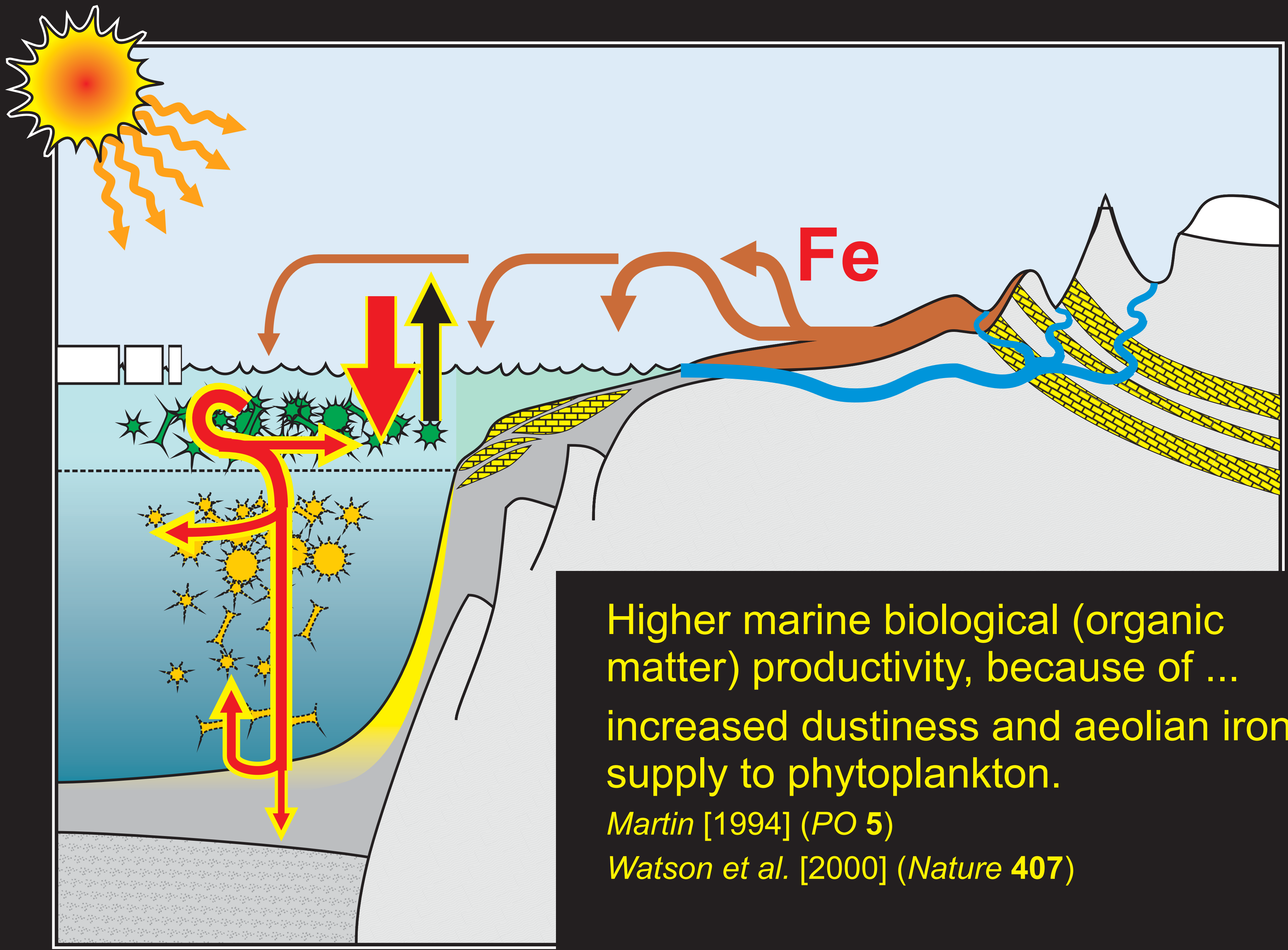
Changes in ocean circulation, particularly wind-driven upwelling, stratification, Atlantic meridional overturning; variously affecting biological and solubility pumps of CO_2.

Sarmiento and Toggweiler [1984] (*Nature* **308**)

Toggweiler [1999] (*PO* **14**)



Glacial-interglacial CO_2 audit
CO_2 terms
CO_2 (ppm)
LOSU
SST
+26 (21/30)
High
sea-level
salinity
non-salinity effects
-6 (-7/-5)
-7 (-9/-6)
High
terrestrial biosphere
-22 (-35/-12)
High
partial linear sum:
High LOSU terms
-9 (-30/6)
High
ocean circulation
AMOC strength
SO stratification
whole ocean
12 (7/15)
33 (31/35)
27 (3/57)
Med-Low
?
glacial→interglacial amplitude (20→0 ka)
deglacial transition (17→11 ka)
CO_2 change (ppm)
-40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90 100



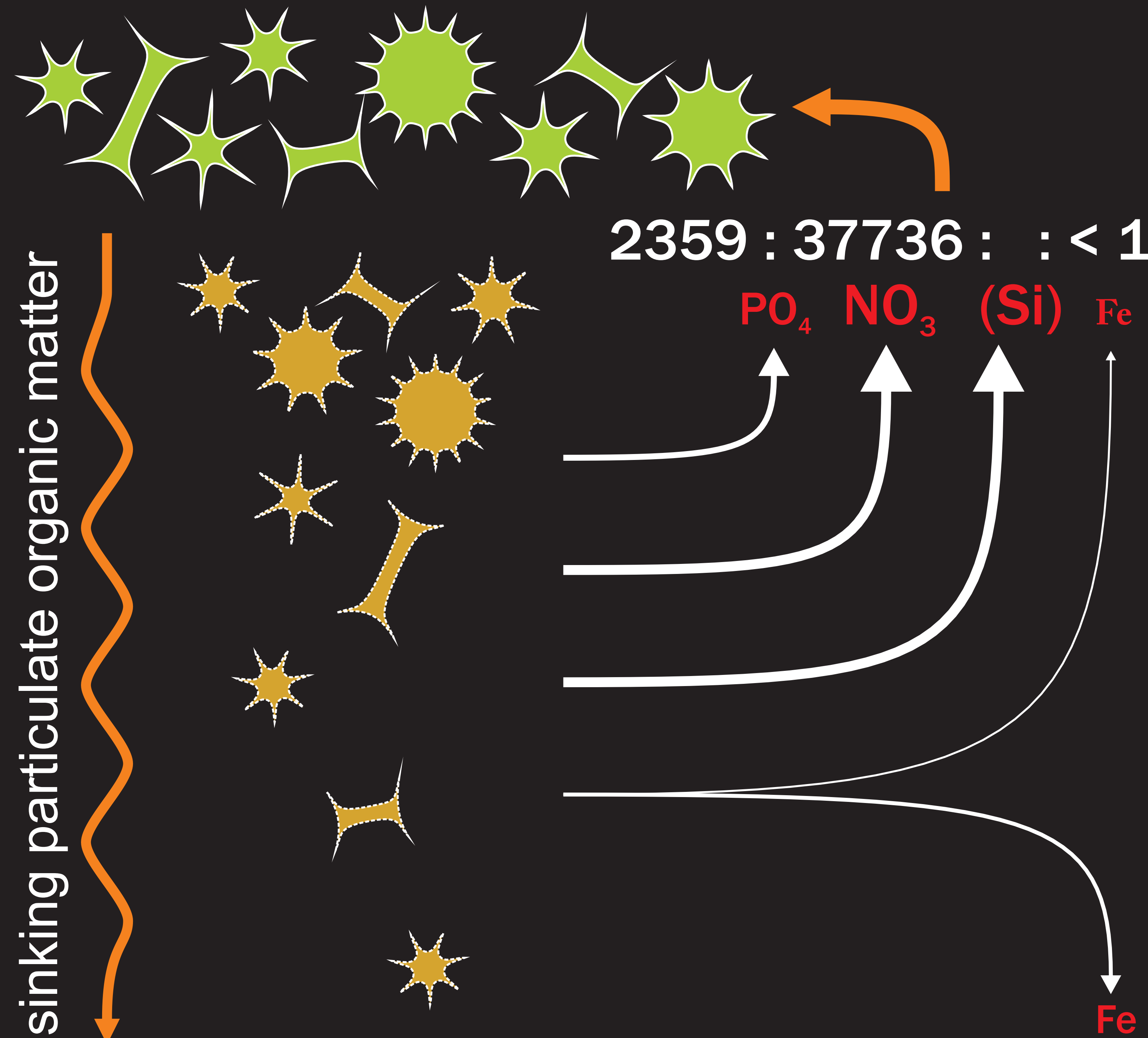
Higher marine biological (organic matter) productivity, because of ...

increased dustiness and aeolian iron supply to phytoplankton.

Martin [1994] (*PO* **5**)

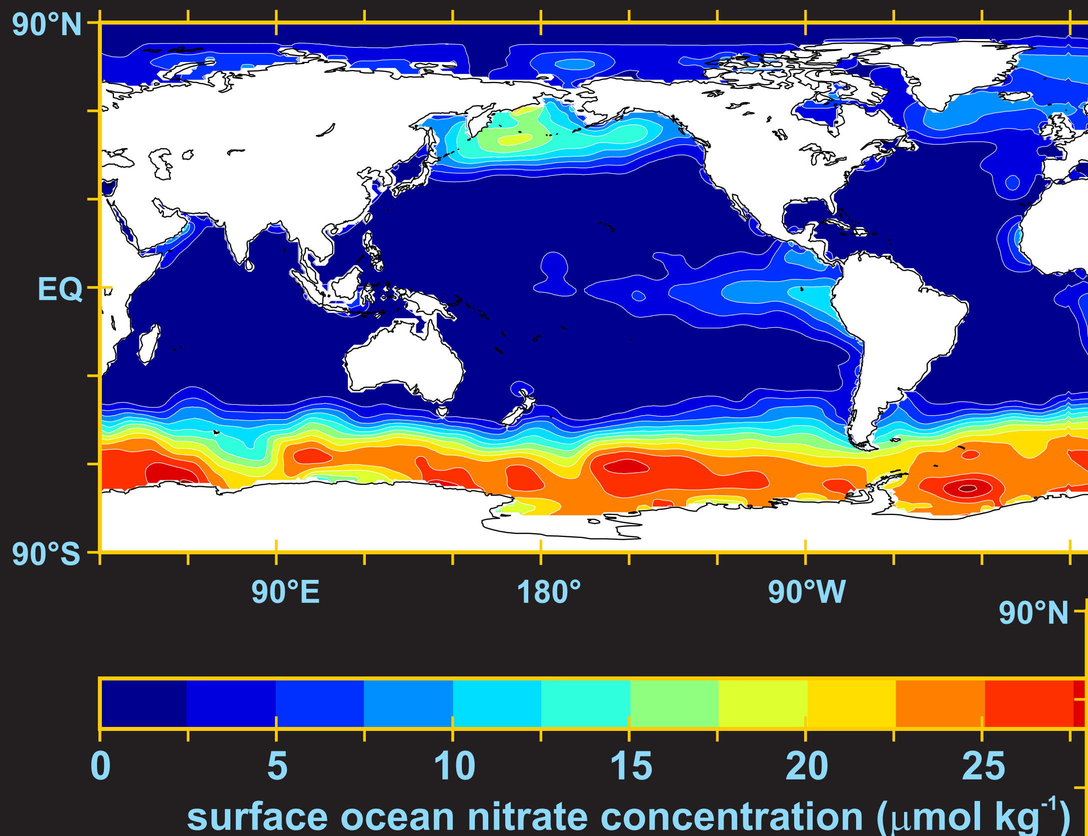
Watson et al. [2000] (*Nature* **407**)

The 'biological pump' in the ocean

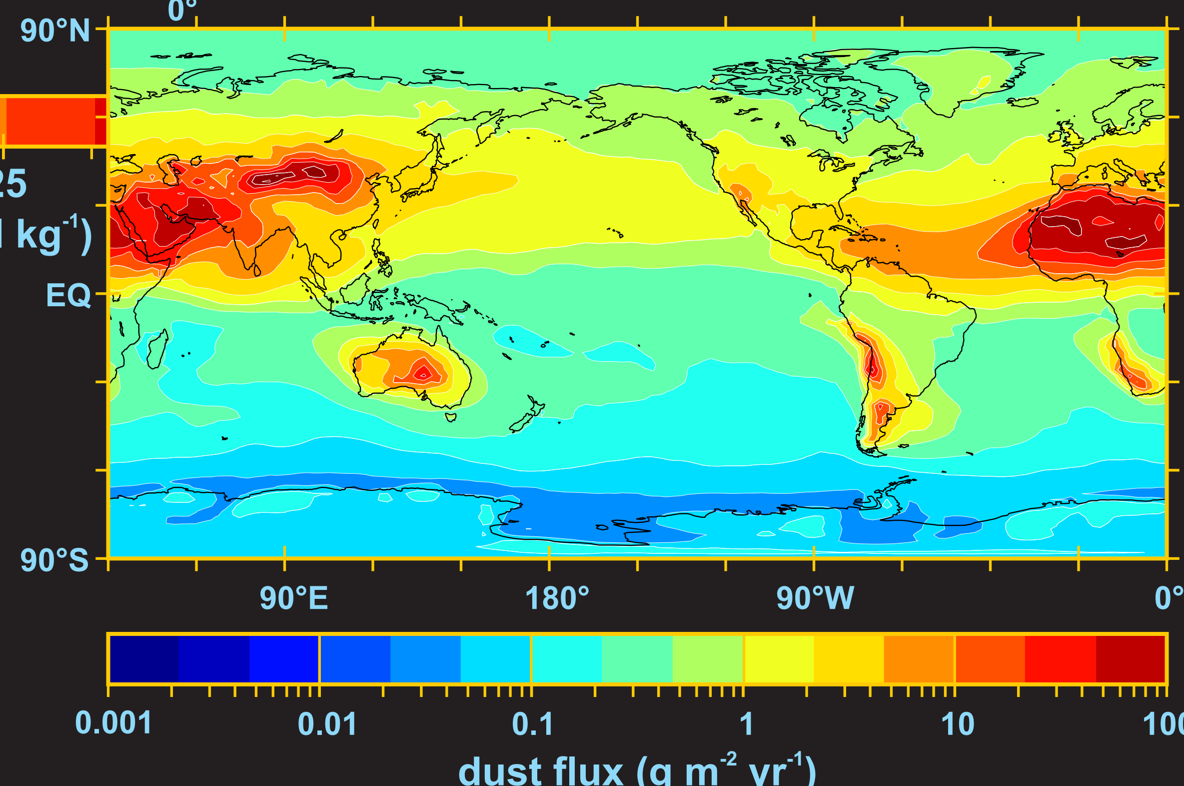


In oxic (oxygenated) seawater, Fe is only sparingly soluble, and tends to be 'scavenged' by particles and

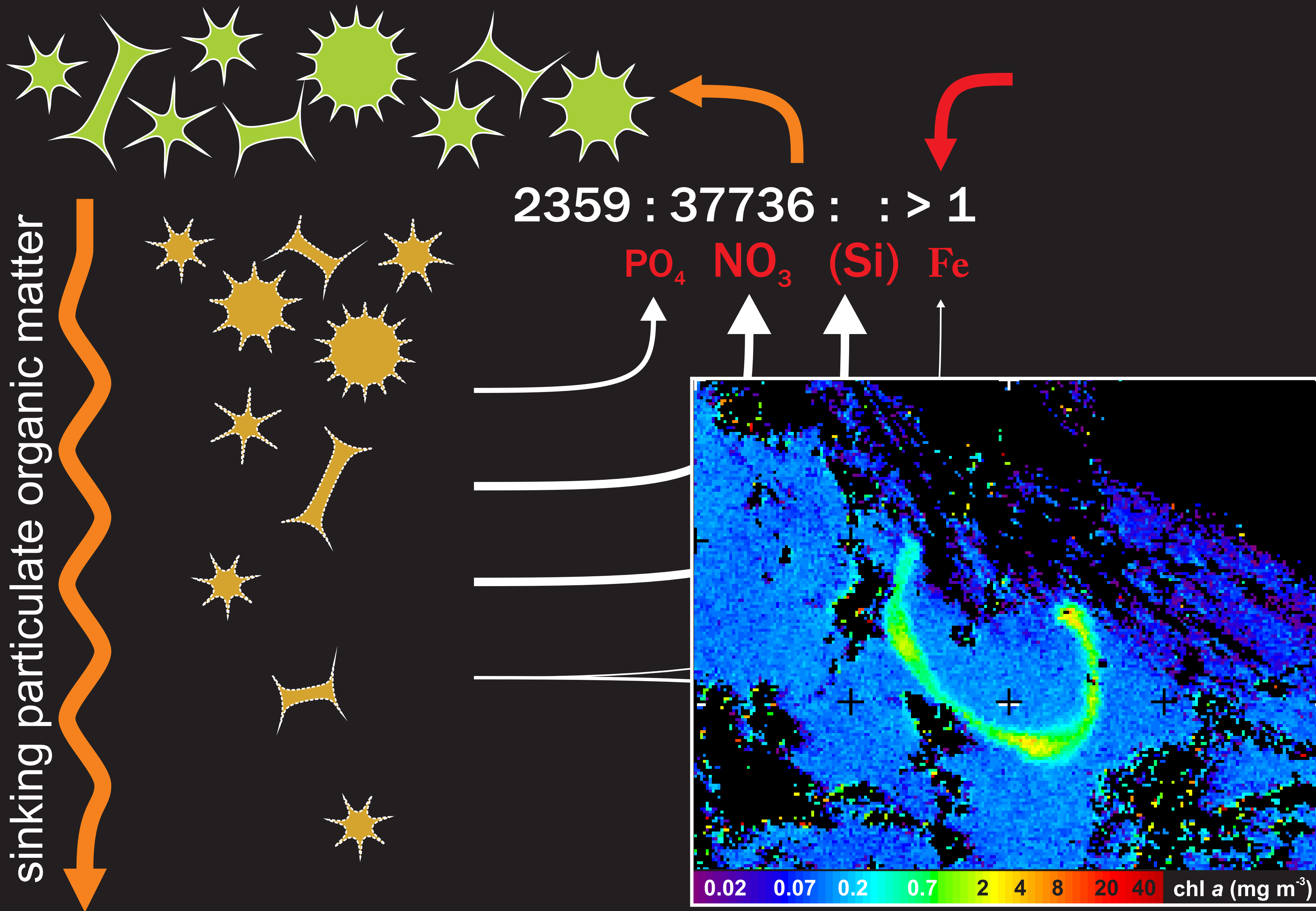
Global distribution of near-surface (30 m depth) ocean nitrate concentrations [*Conkright et al.*, 1994]



Model-simulated annual mean dust flux to the Earth's surface [*Ginoux et al.*, 2001]

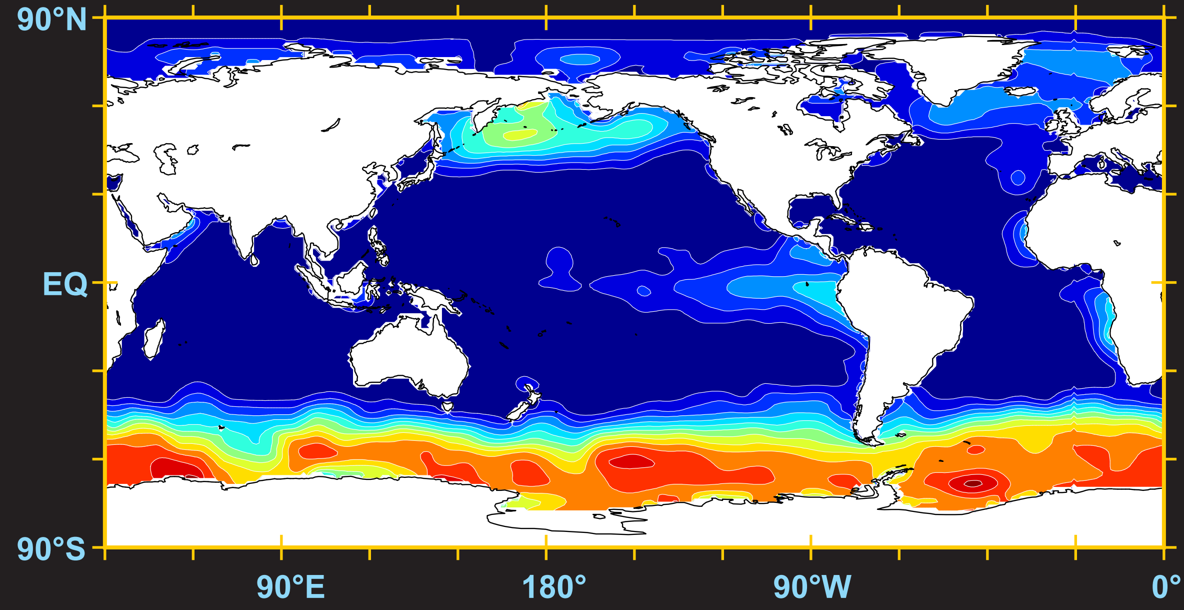


The 'biological pump' in the ocean

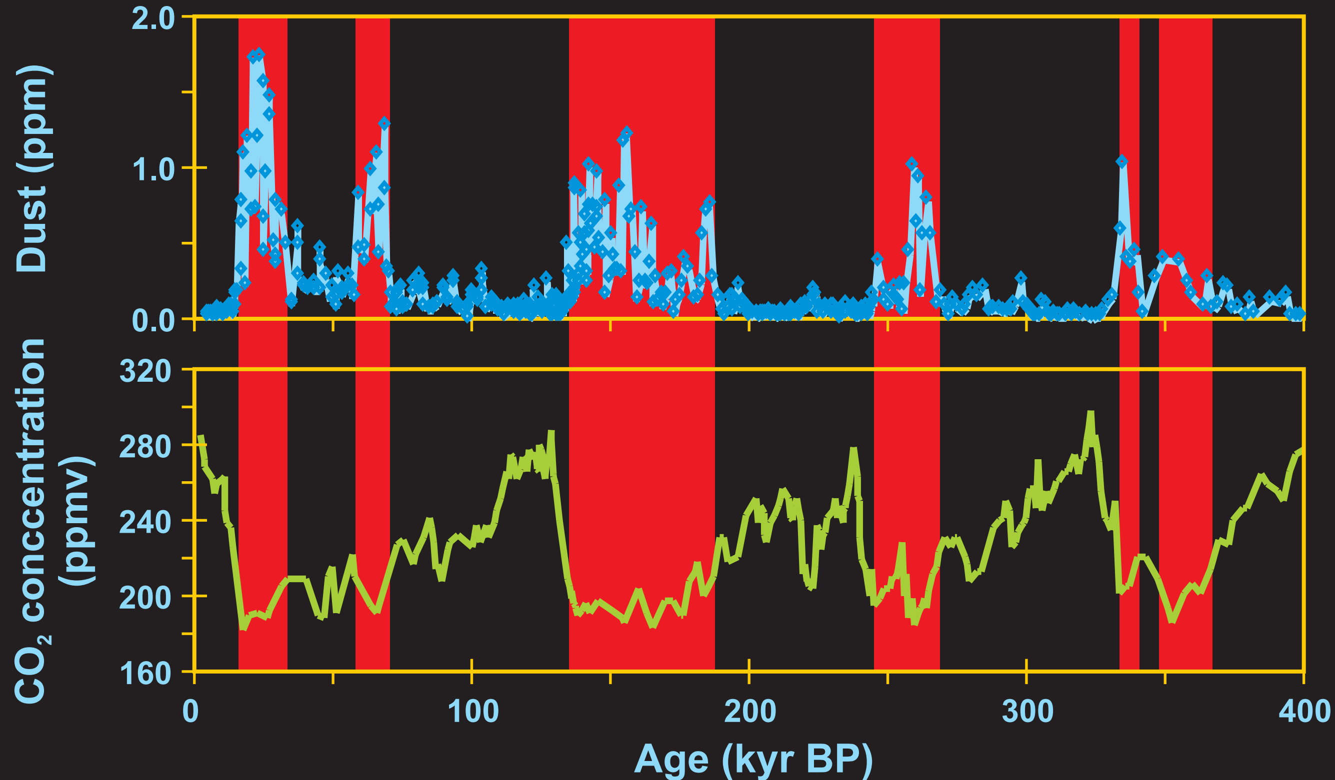


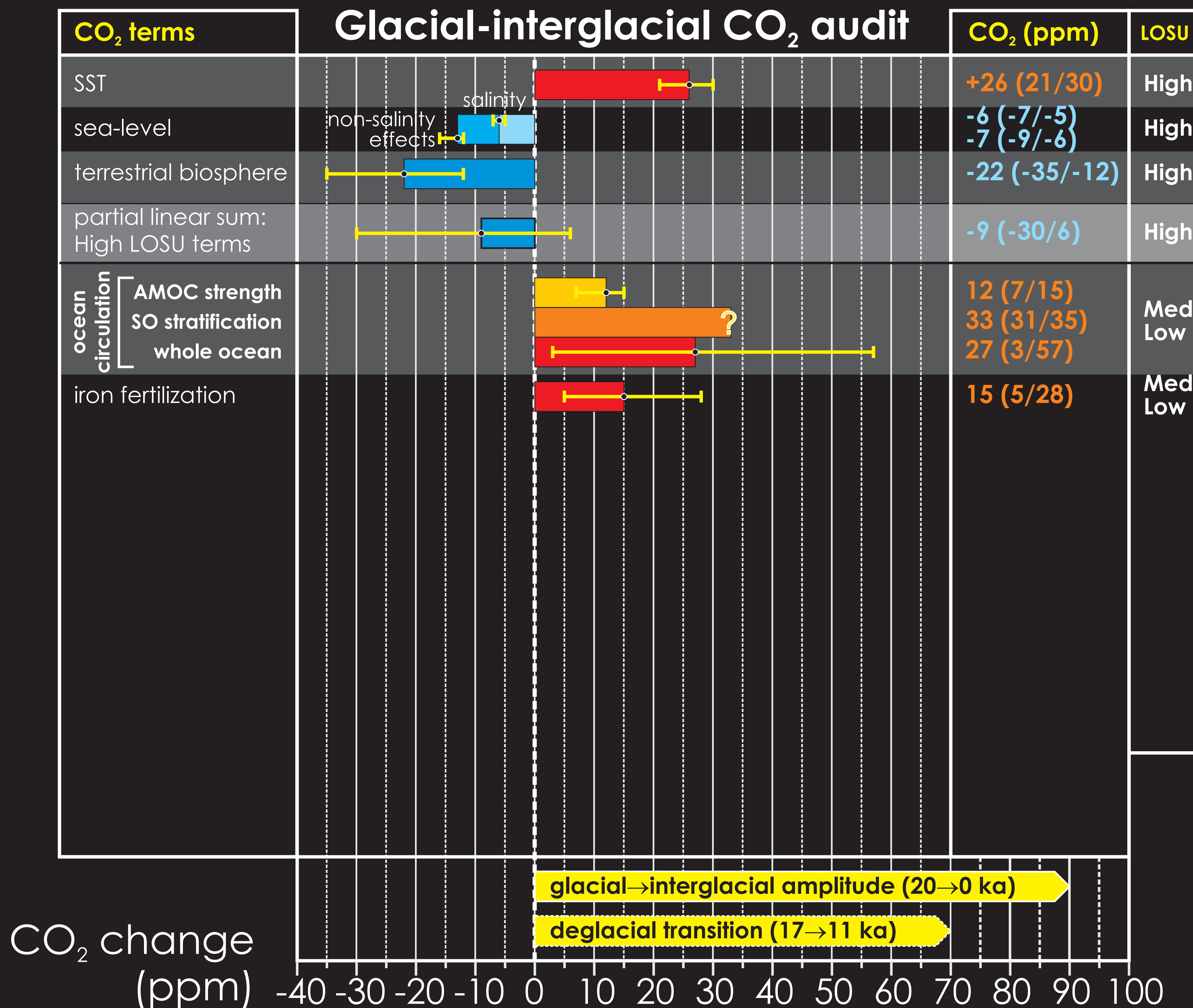
SeaWiFS data provided by NASA DAAC/GSFC (copyright of Orbital Imaging Corps and the NASA SeaWiFS project) and processed at CCMS-PML.

Global distribution of near-surface (30 m depth) ocean nitrate concentrations [*Conkright et al.*, 1994]

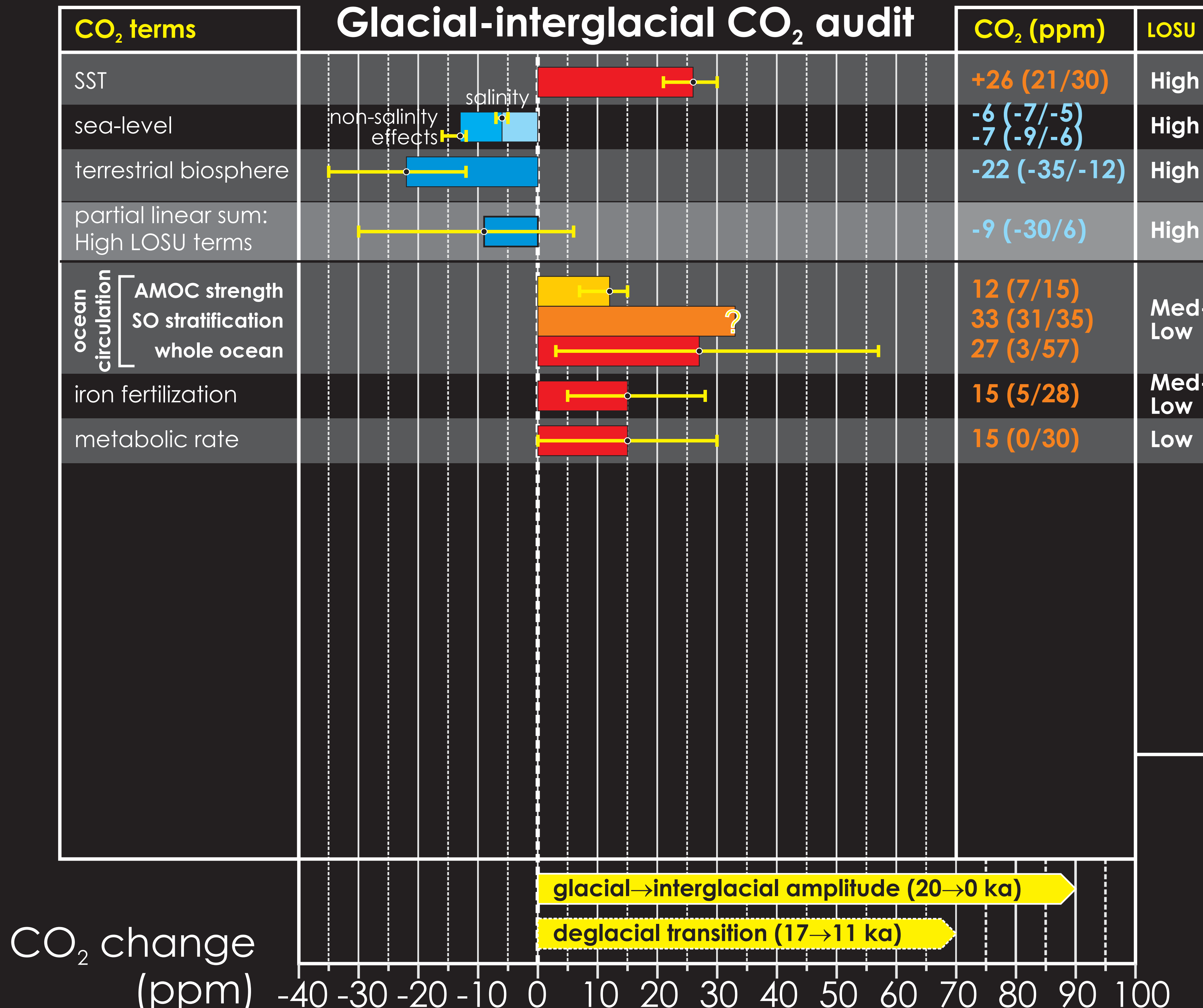


Dust concentration (blue, top) and CO_2 content of air bubbles (green, bottom) trapped in the ice, both from the Vostok ice core, Antarctica. [*Petit et al.*, 1999]

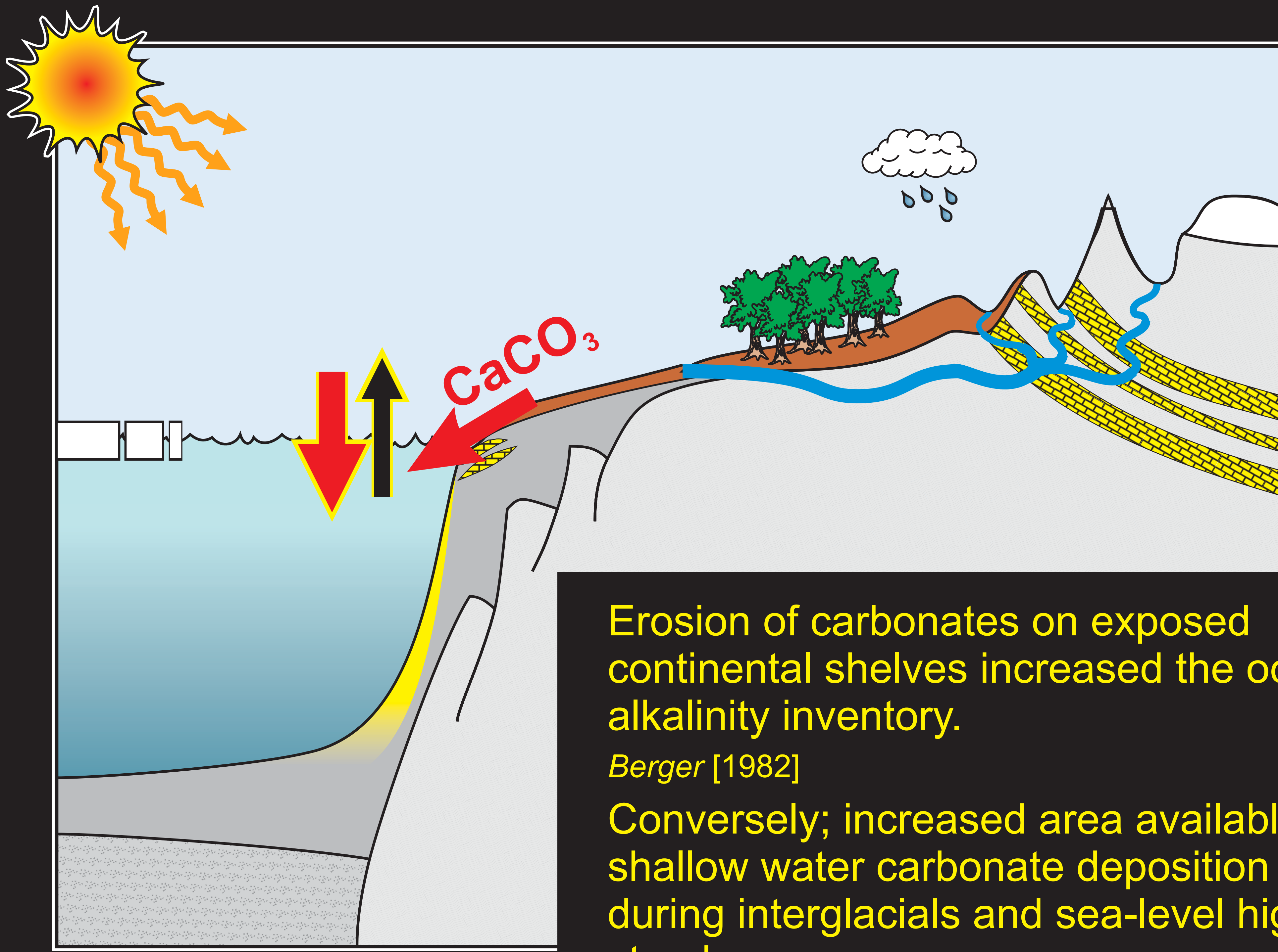




CO2 terms
Glacial-interglacial CO2 audit
CO2 (ppm)
LOSU
SST
+26 (21/30)
High
sea-level
salinity
non-salinity effects
-6 (-7/-5)
-7 (-9/-6)
High
terrestrial biosphere
-22 (-35/-12)
High
partial linear sum: High LOSU terms
-9 (-30/6)
High
ocean circulation
AMOC strength
SO stratification
whole ocean
12 (7/15)
33 (31/35)
27 (3/57)
Med-Low
iron fertilization
15 (5/28)
Med-Low
glacial→interglacial amplitude (20→0 ka)
deglacial transition (17→11 ka)
CO2 change (ppm)
-40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90 100



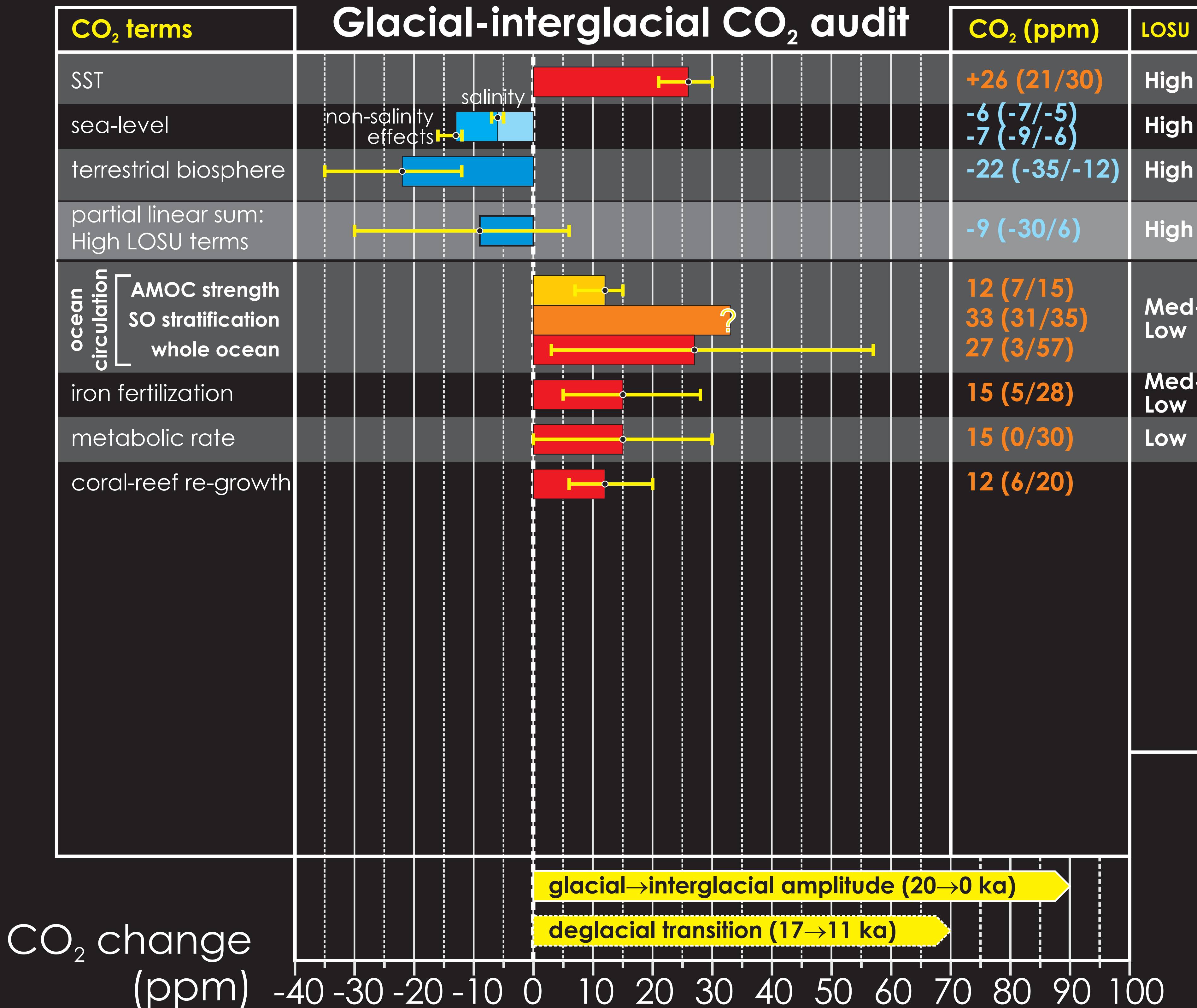
Glacial-interglacial CO_2 audit
CO_2 terms
CO_2 (ppm)
LOSU
SST
+26 (21/30)
High
sea-level
salinity
non-salinity effects
-6 (-7/-5)
-7 (-9/-6)
High
terrestrial biosphere
-22 (-35/-12)
High
partial linear sum: High LOSU terms
-9 (-30/6)
High
ocean circulation
AMOC strength
12 (7/15)
SO stratification
33 (31/35)
?
whole ocean
27 (3/57)
Med-Low
iron fertilization
15 (5/28)
Med-Low
metabolic rate
15 (0/30)
Low
glacial→interglacial amplitude (20→0 ka)
deglacial transition (17→11 ka)
CO_2 change (ppm)
-40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90 100



Erosion of carbonates on exposed continental shelves increased the ocean alkalinity inventory.

Berger [1982]

Conversely; increased area available for shallow water carbonate deposition during interglacials and sea-level high stands.



Glacial-interglacial CO_2 audit
CO_2 terms
CO_2 (ppm)
LOSU
SST
+26 (21/30)
High
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non-salinity effects
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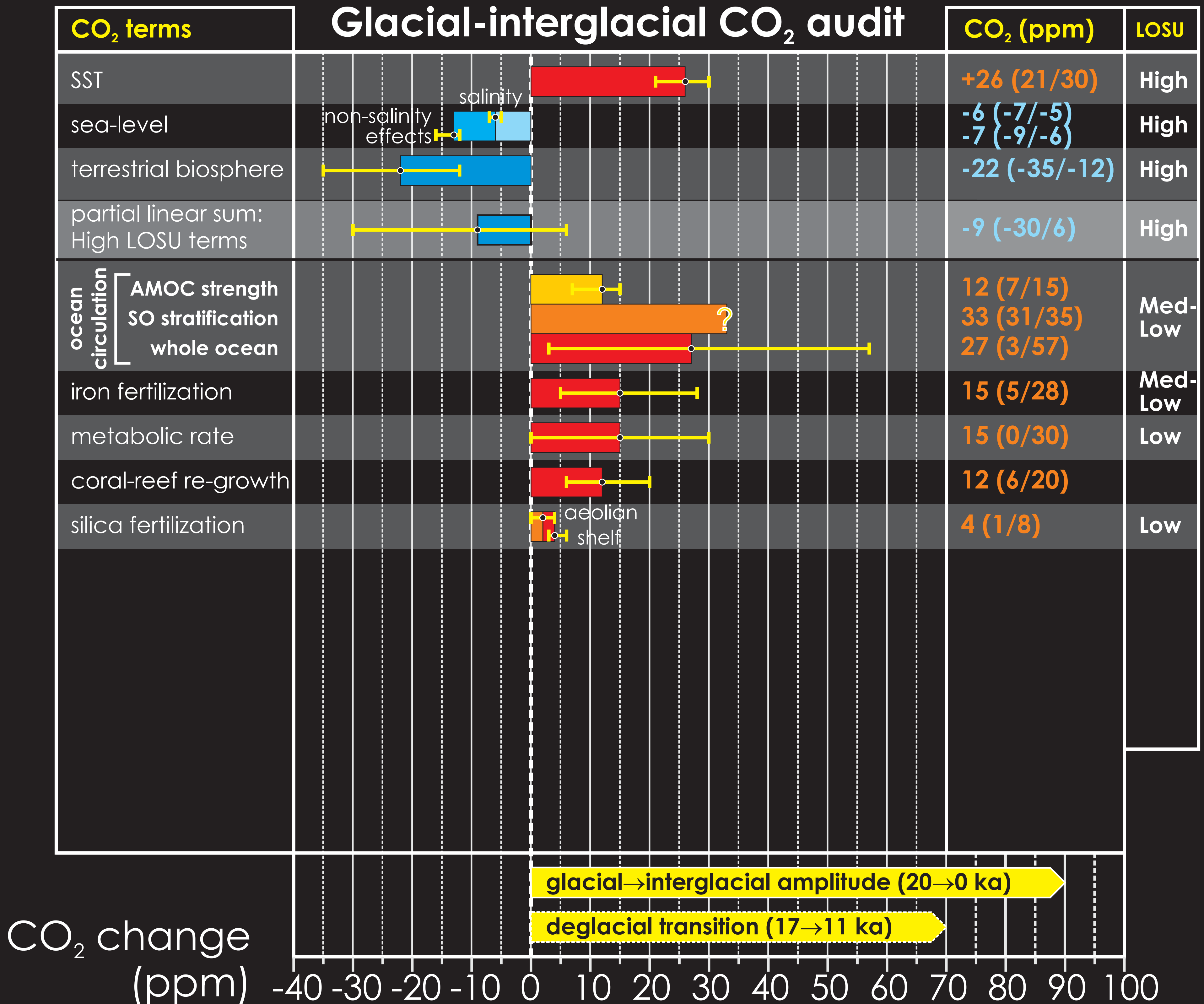
Low
coral-reef re-growth
12 (6/20)
glacial→interglacial amplitude (20→0 ka)
deglacial transition (17→11 ka)
CO_2 change (ppm)
-40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90 100


Glacial-interglacial CO_2 audit
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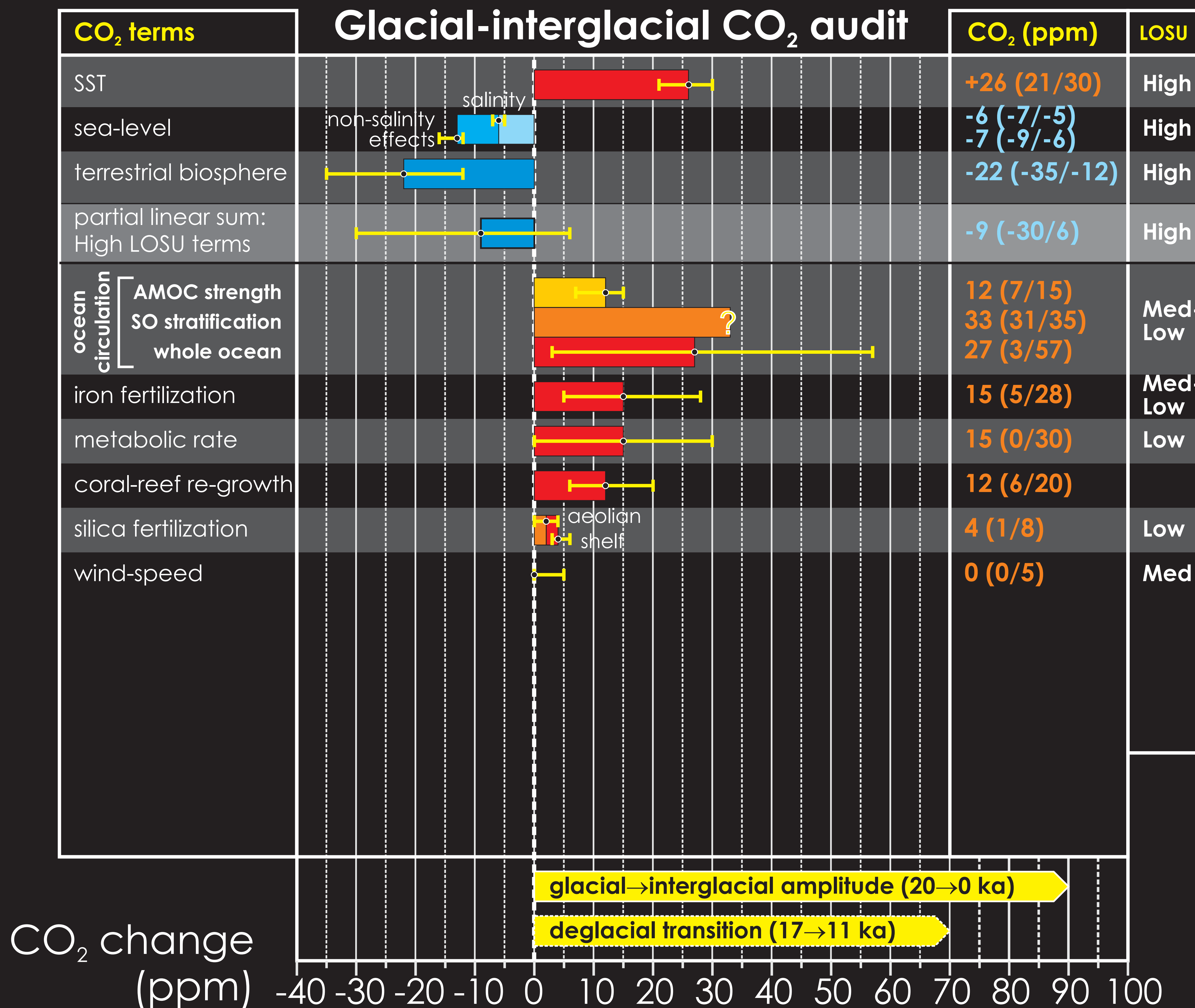
Med-Low
metabolic rate
15 (0/30)
Low
coral-reef re-growth
12 (6/20)
silica fertilization
aeolian
shelf
4 (1/8)
Low
glacial→interglacial amplitude (20→0 ka)
deglacial transition (17→11 ka)
CO_2 change (ppm)
-40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90 100


Glacial-interglacial CO_2 audit
CO_2 terms
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LOSU
SST
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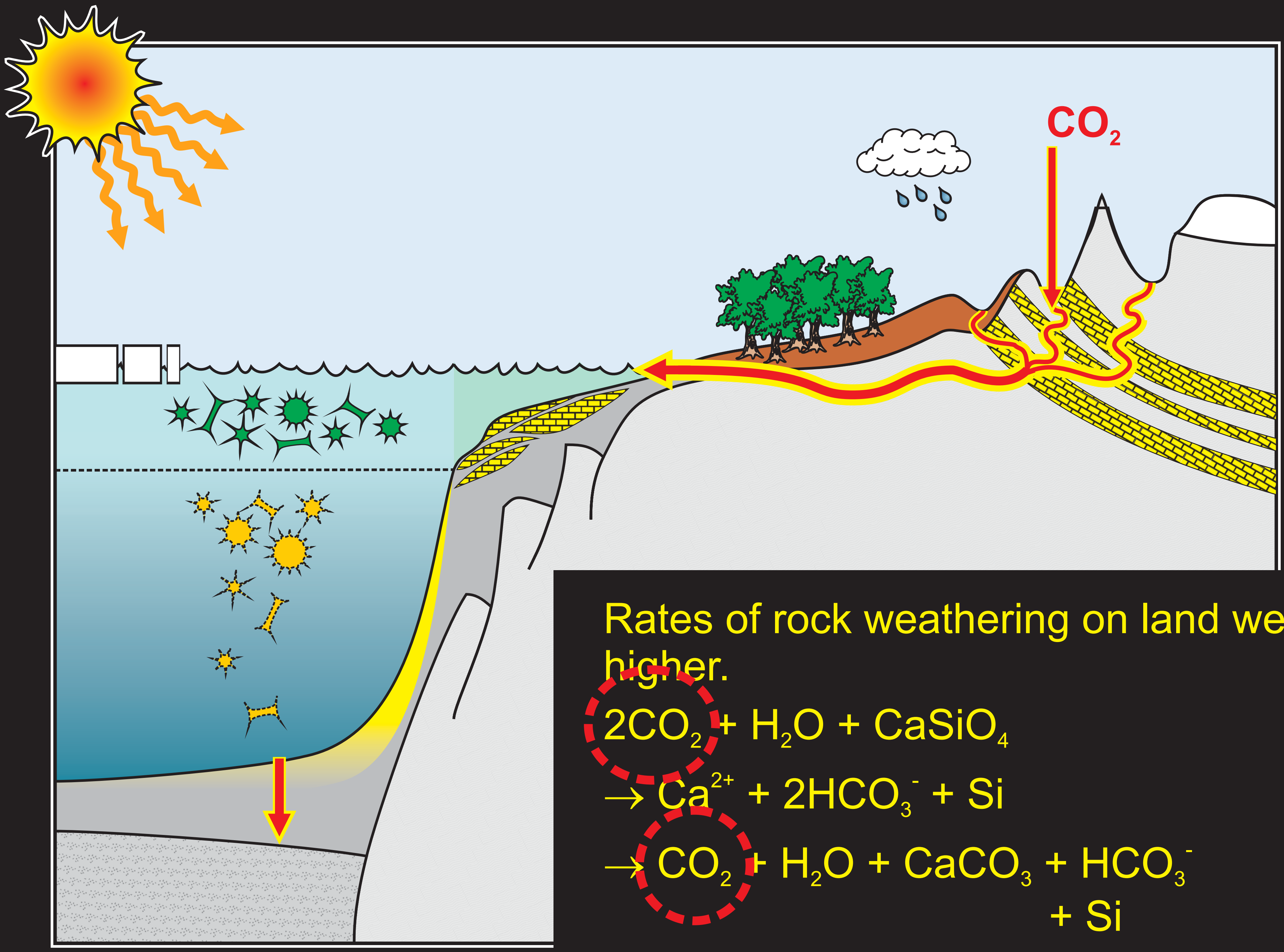
Med
glacial→interglacial amplitude (20→0 ka)
deglacial transition (17→11 ka)
CO_2 change (ppm)
-40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90 100



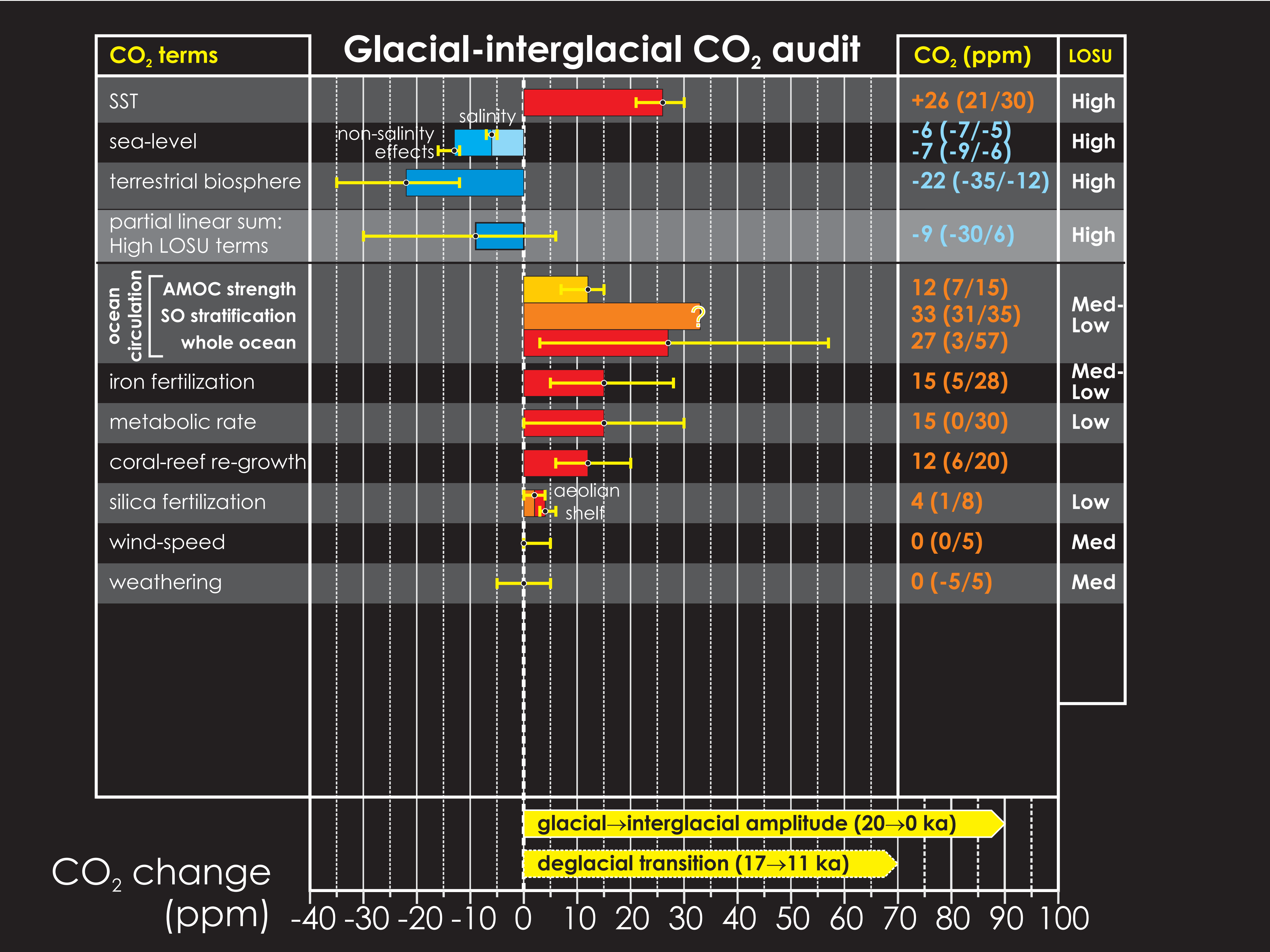
Rates of rock weathering on land were higher.

$2CO_2 + H_2O + CaSiO_4$

$\rightarrow Ca^{2+} + 2HCO_3^- + Si$

$\rightarrow CO_2 + H_2O + CaCO_3 + HCO_3^-$
$+ Si$

Munhoven and Francois [1994]



Glacial-interglacial CO_2 audit
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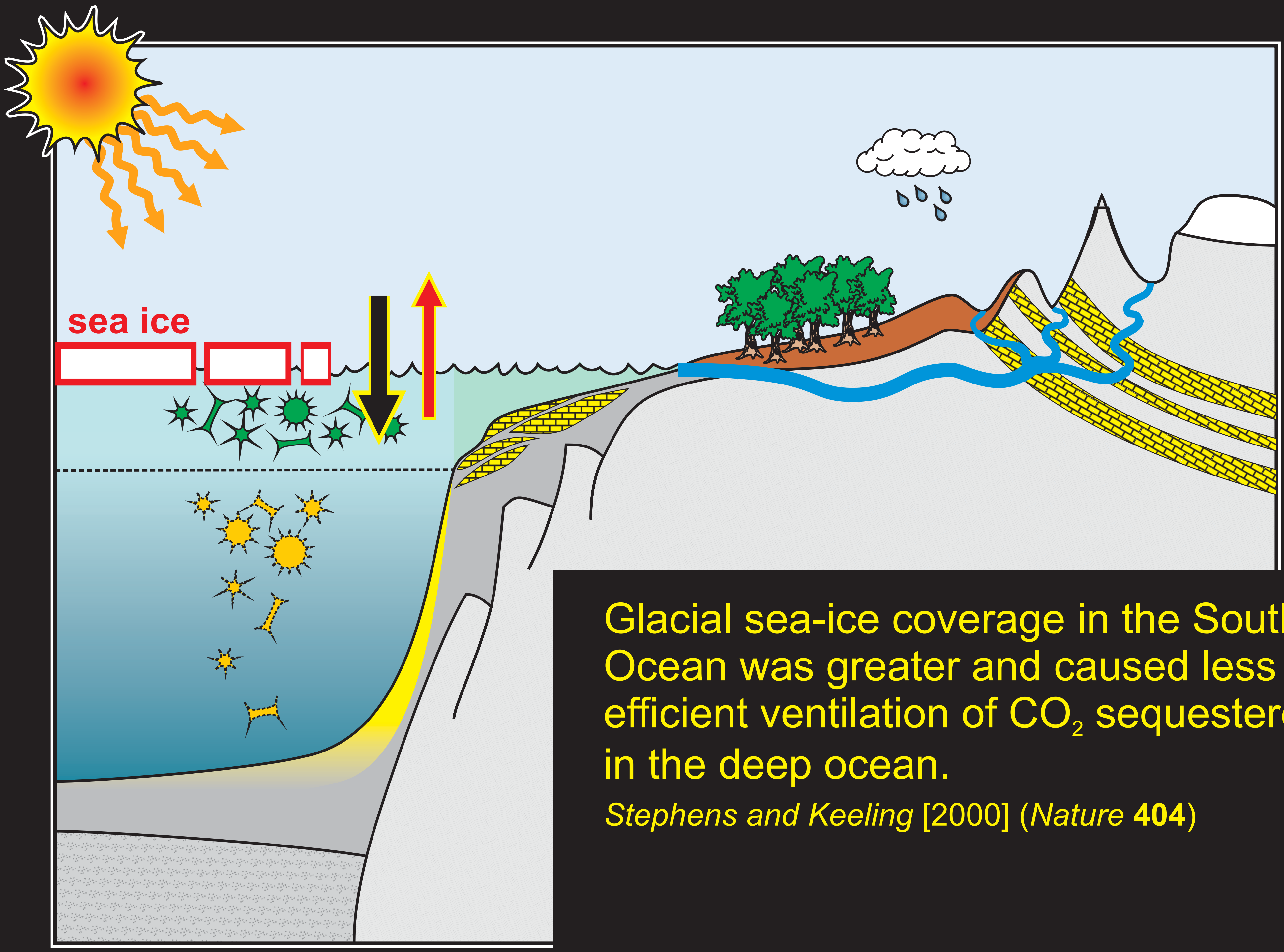
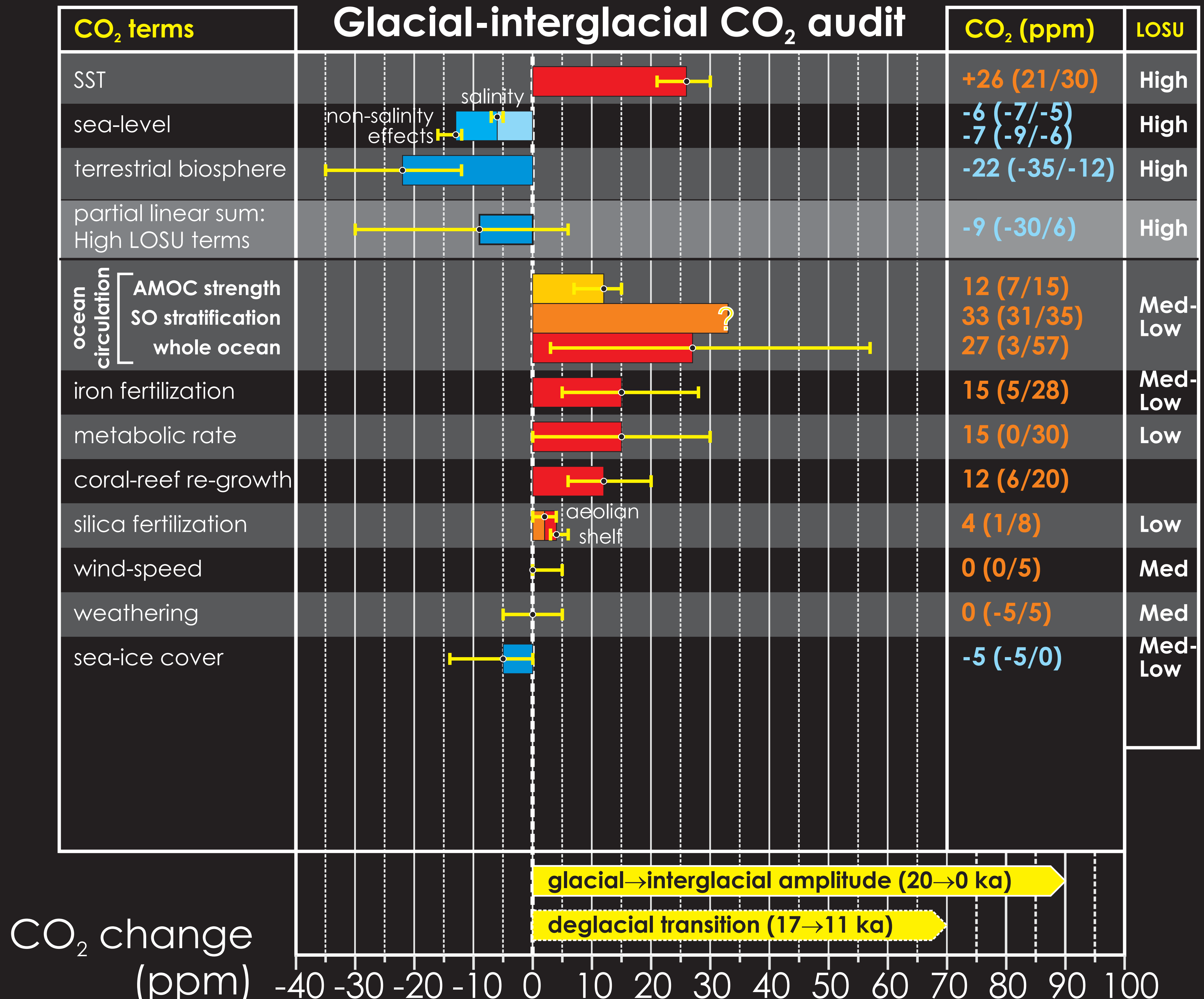
4 (1/8)
Low
wind-speed
0 (0/5)
Med
weathering
0 (-5/5)
Med
glacial→interglacial amplitude (20→0 ka)
deglacial transition (17→11 ka)
CO_2 change (ppm)
-40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90 100



Glacial sea-ice coverage in the Southern Ocean was greater and caused less efficient ventilation of CO_2 sequestered in the deep ocean.

Stephens and Keeling [2000] (*Nature* **404**)



Glacial-interglacial CO_2 audit
CO_2 terms
CO_2 (ppm)
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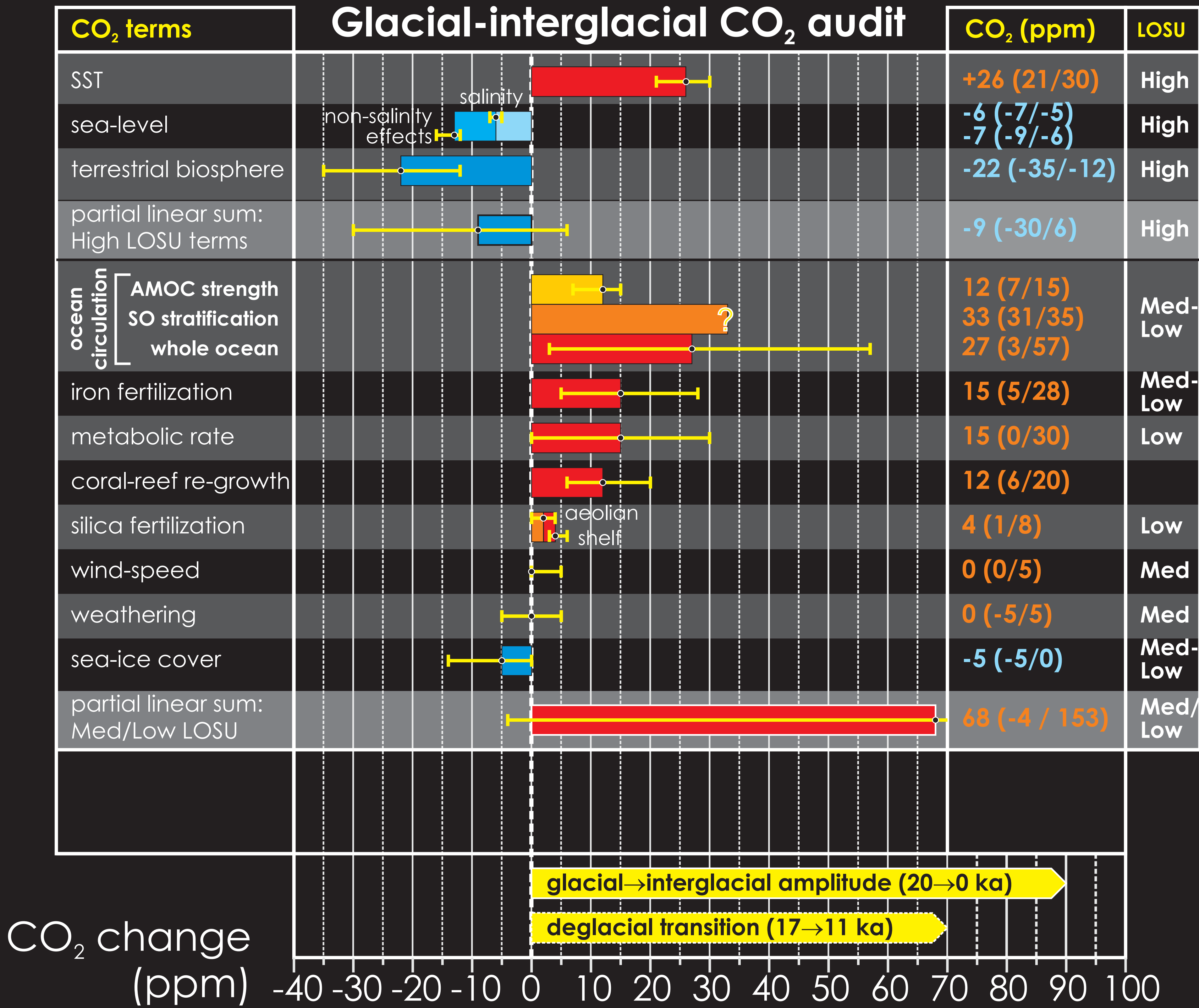
silica fertilization
aeolian
shelf
4 (1/8)
Low
wind-speed
0 (0/5)
Med
weathering
0 (-5/5)
Med
sea-ice cover
-5 (-5/0)
Med-Low
glacial→interglacial amplitude (20→0 ka)
deglacial transition (17→11 ka)
CO_2 change (ppm)
-40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90 100



Glacial-interglacial CO2 audit
CO2 terms
CO2 (ppm)
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silica fertilization
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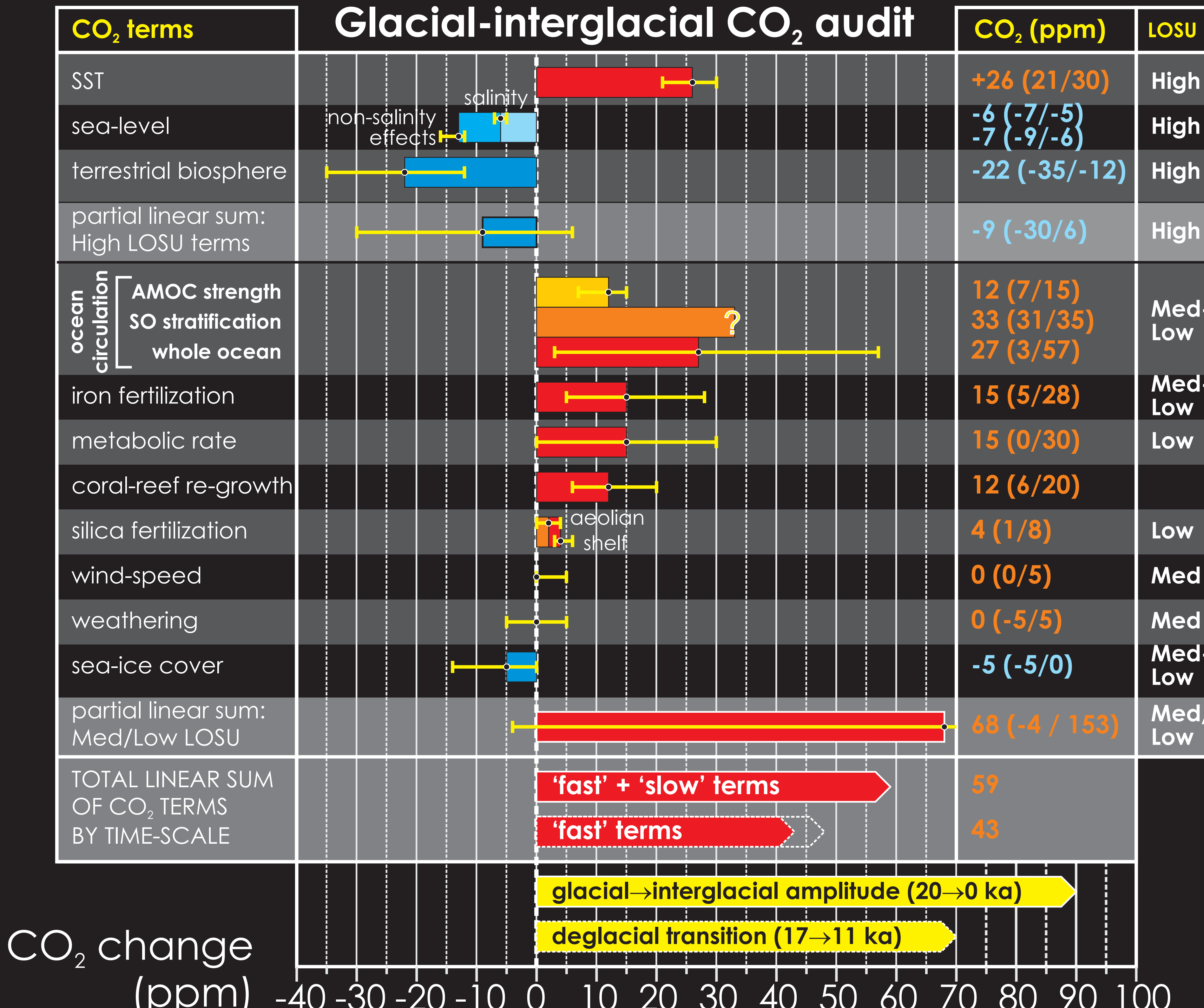
4 (1/8)
Low
wind-speed
0 (0/5)
Med
weathering
0 (-5/5)
Med
sea-ice cover
-5 (-5/0)
Med-Low
partial linear sum: Med/Low LOSU
68 (-4 / 153)
Med/Low
glacial→interglacial amplitude (20→0 ka)
deglacial transition (17→11 ka)
CO2 change (ppm)
-40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90 100



Glacial-interglacial CO_2 audit
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Low
wind-speed
0 (0/5)
Med
weathering
0 (-5/5)
Med
sea-ice cover
-5 (-5/0)
Med-Low
partial linear sum: Med/Low LOSU
68 (-4 / 153)
Med/Low
TOTAL LINEAR SUM OF CO_2 TERMS BY TIME-SCALE
'fast' + 'slow' terms
59
'fast' terms
43
glacial→interglacial amplitude (20→0 ka)
deglacial transition (17→11 ka)
CO_2 change (ppm)
-40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90 100