Glacial-Interglacial CO_2 cycles: A review of concepts

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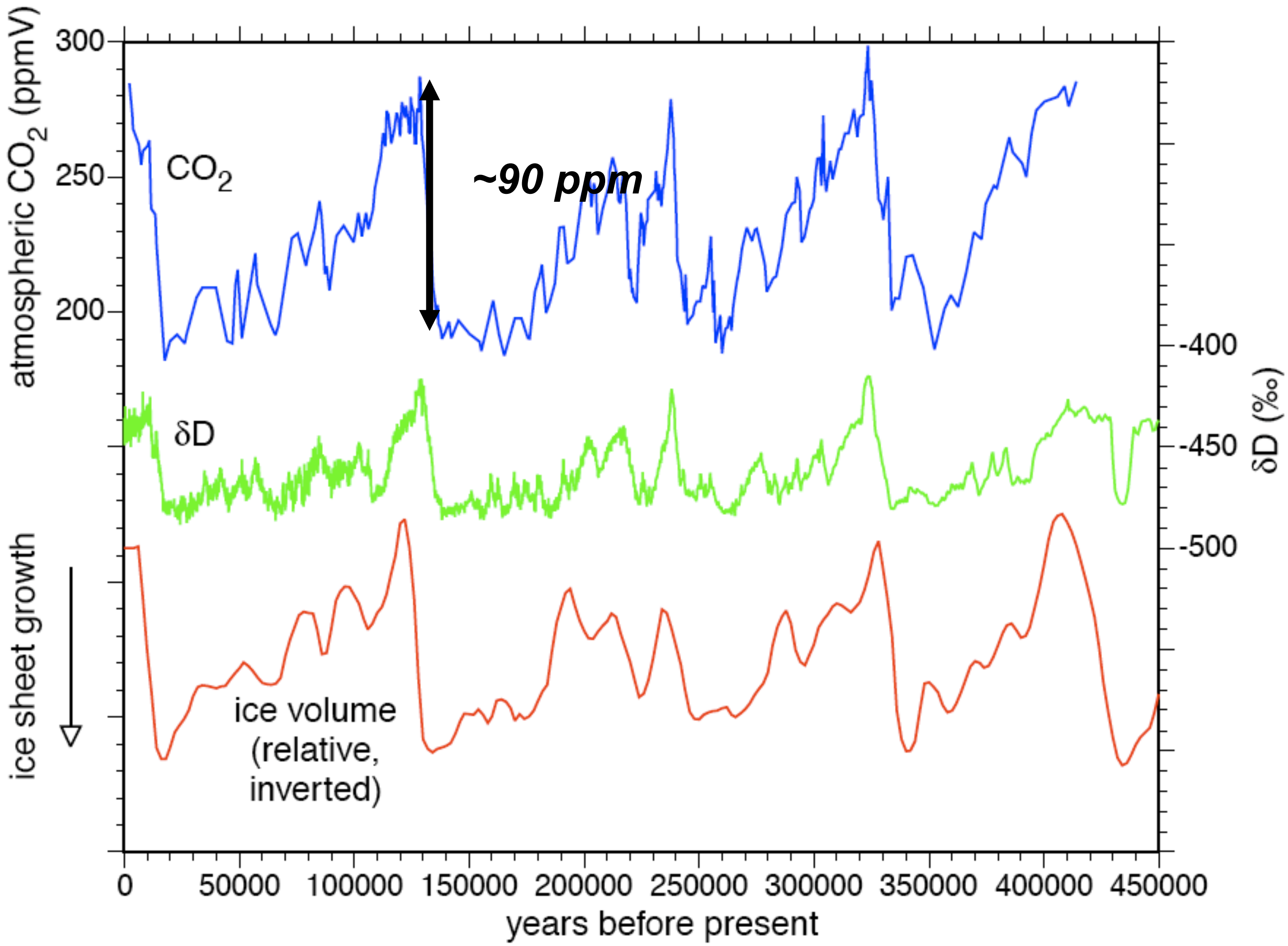
Ice-age climate and CO_2 cycles



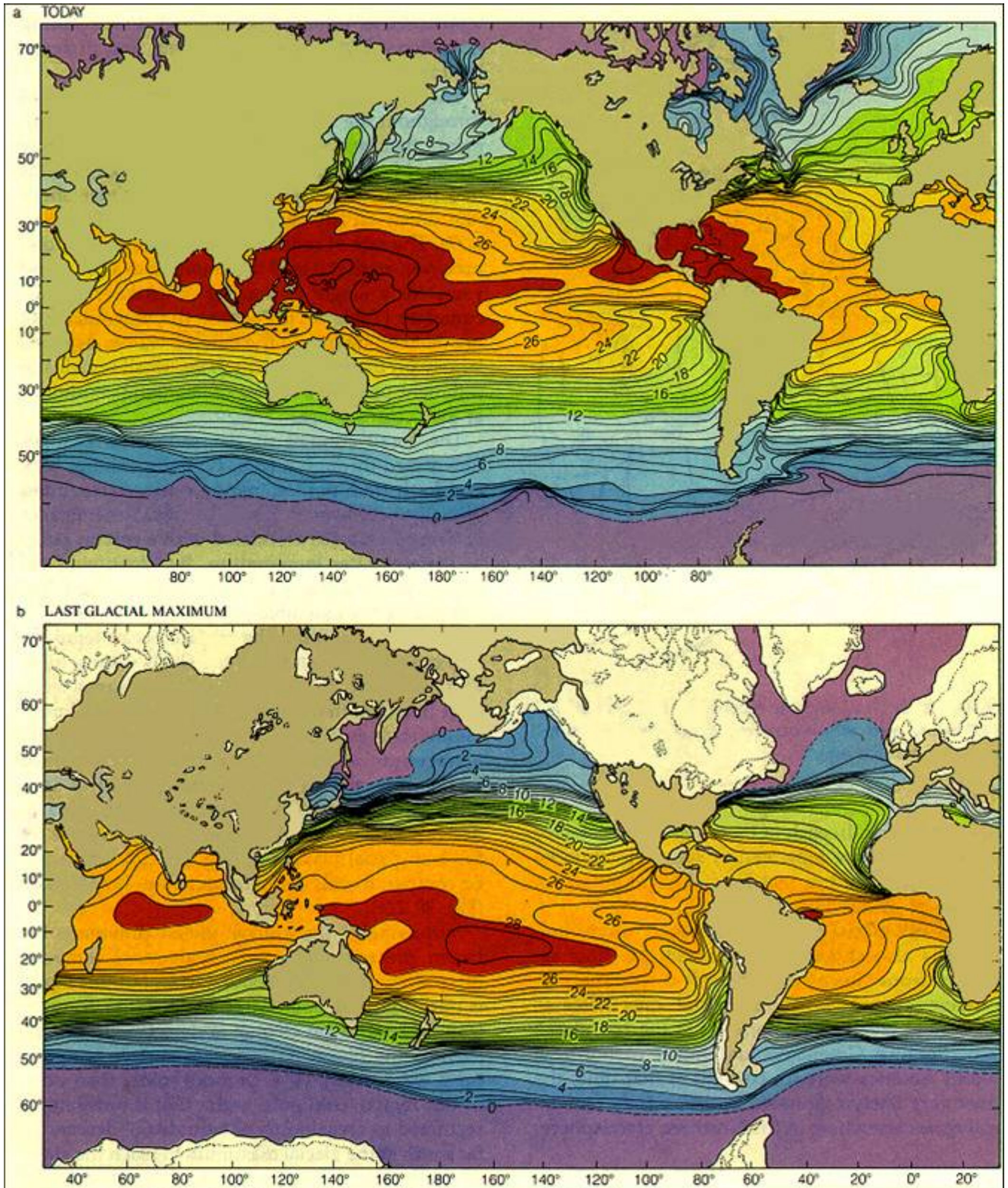


FIGURE 20.22 (*a*) Map showing modern sea-surface temperatures (°C) during August. (*b*) Map showing reconstructed August sea-surface temperatures during the last glacial maximum, about 18,000 years ago. Cold polar water extended far south of its present limit in the North Atlantic, and plumes of cold water flowed westward in the equatorial Pacific and Atlantic. (*Source:* After CLIMAP Project Members, 1976.)

Carbon in the Glacial Terrestrial Biosphere

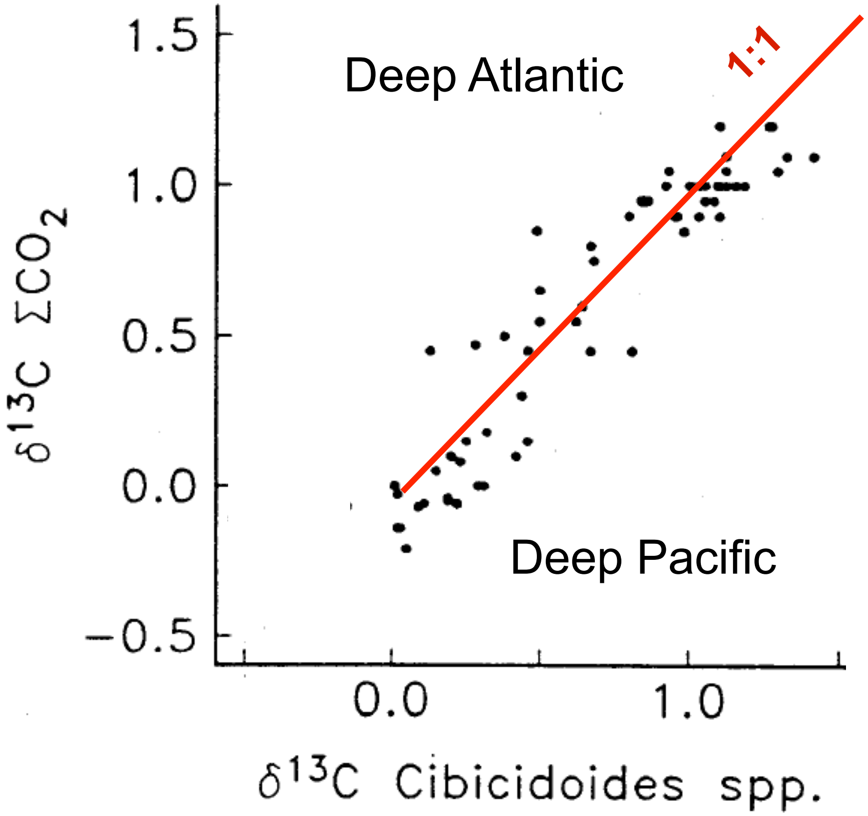
1) More ice covered areas
- less carbon
2) Drier climate/expanded deserts
- less carbon
3) Forests -> grassland
- less carbon

Altogether less Carbon on land,
It too must have gone into ocean.

Terrestrial estimates 700-1400 GtC

Organic carbon low 13C/12C ratio
Recorded in marine sediments
--> only 300-700 GtC input

Water mass proxy: $\delta^{13}C$



(benthic foraminifera)

Similar to $\delta^{18}O$, benthic foraminifera also record the $\delta^{13}C$ of the DIC in which they grow. They can thus be used to infer changes in deep water PO_4 concentration.

Atmosphere-Ocean Balance

Recall from Matt's lecture

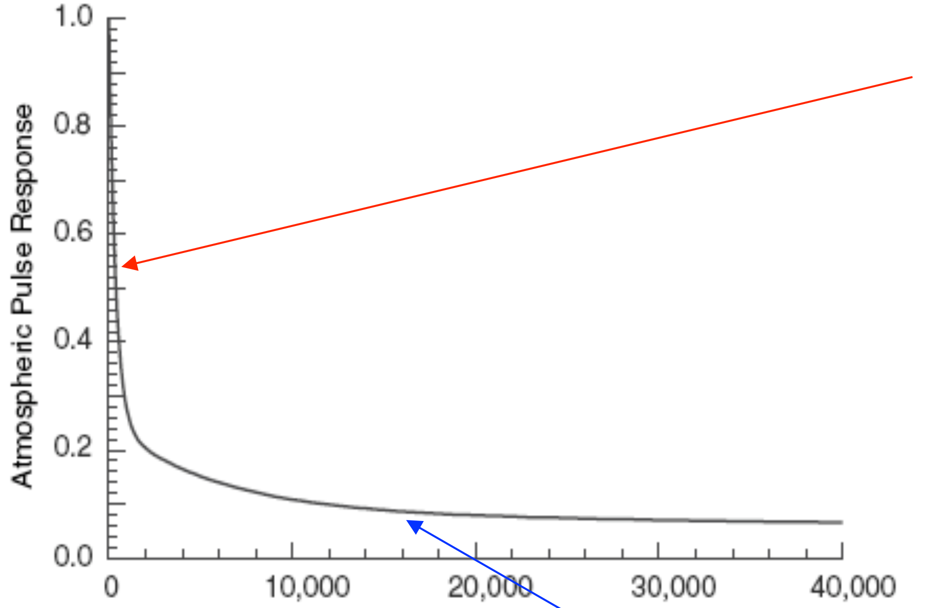
Total C: $$C = C_{oc} + C_{atm}$$

Perturbation: $$\frac{\delta C_{atm}}{\delta C} = \frac{m_a \cdot \delta pCO_2}{m_a \cdot \delta pCO_2 + V \cdot DIC}$$

then $$\frac{\delta C_{atm}}{\delta C} = \frac{1}{\phi}$$

where $$\phi = \frac{V \cdot DIC}{m_a pCO_2} \frac{1}{\gamma_{DIC}} + 1 \approx 7$$ *is ~ the current mean atmosphere-ocean carbon partition*

The fate of terrestrial carbon



1) Dissolved carbonate buffering:

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

$F \sim 85\%$ (for small change in γ_{DIC})

250 ppm ---> 40 ppm
Timescale ~1000 yr

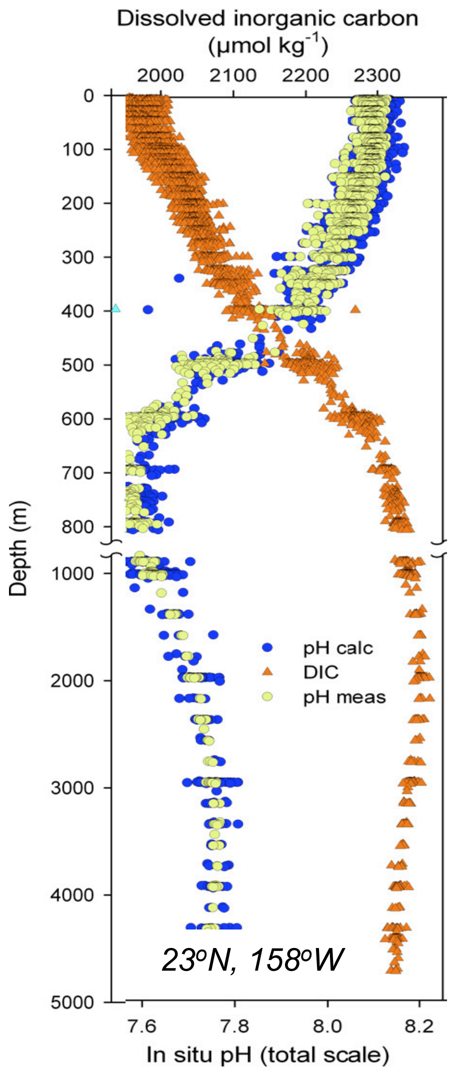
2) Sedimentary CaCO3 buffering:

$H_2O + CO_2 + CaCO_3 \text{--->} Ca^{2+} + 2HCO_3^-$

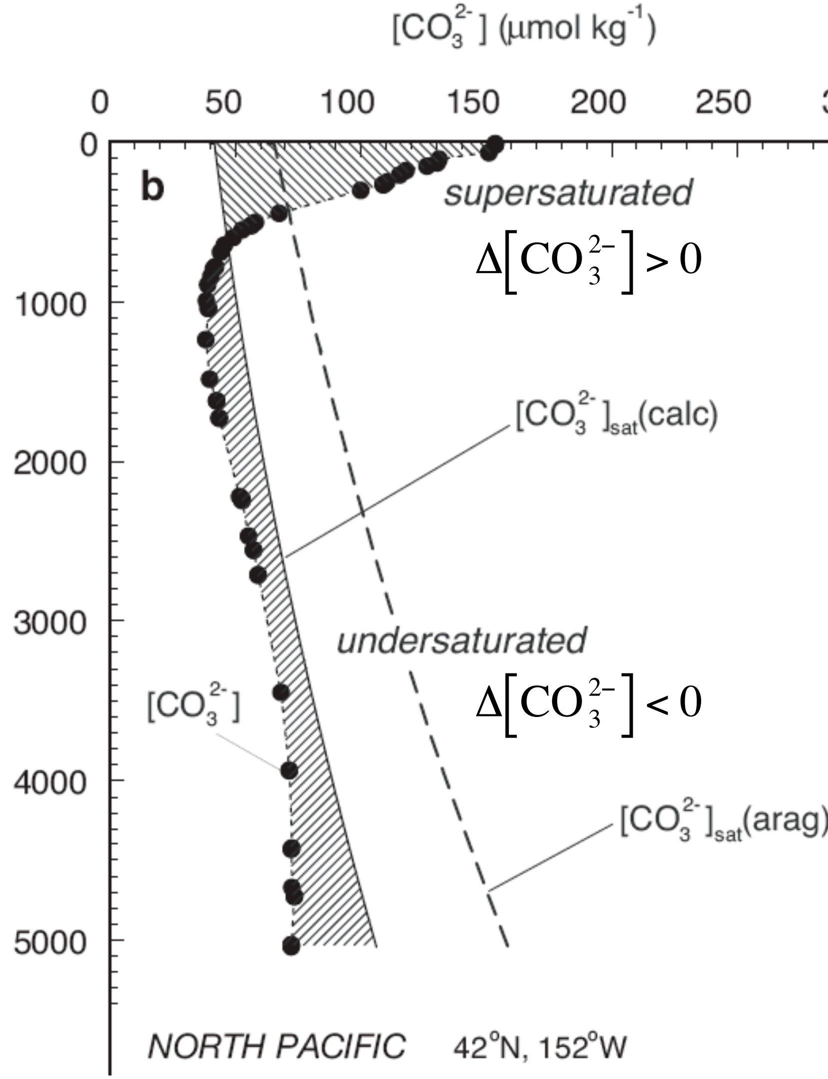
$F \sim 95\%$

40 ppm ---> 15 ppm
Timescale ~10,000yr

Profiles of pH and CO_3^{2-}



Dore et al. [2009]

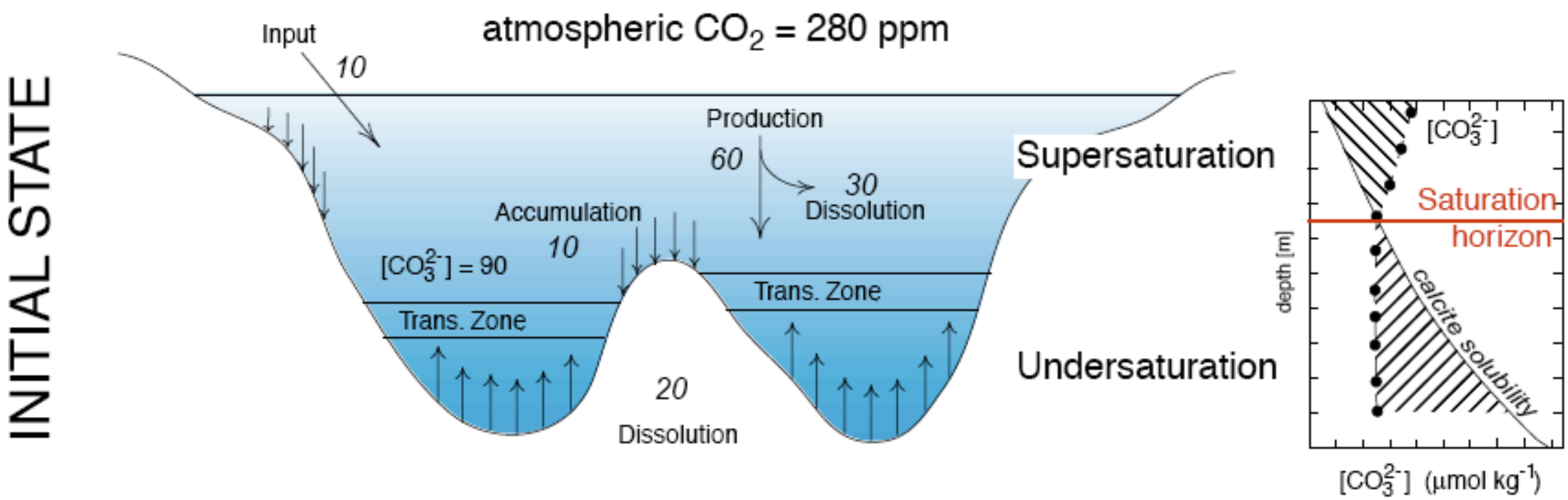


Sarmiento and Gruber [2006]

Respiration in the deep ocean shifts the acid-base balance toward lower pH and CO_3 ion.

Together with the increasing solubility of $CaCO_3$ with pressure, this natural ocean acidification prevents loss of CaCO3 to deep sediments, which is the main sink in the ocean's alkalinity budget.

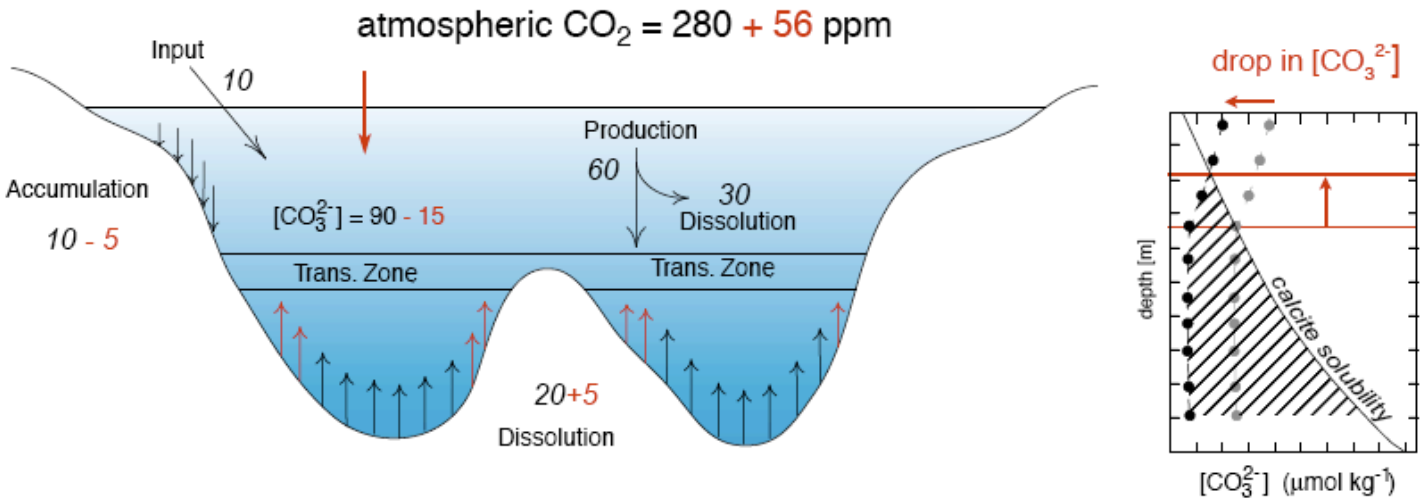
Alkalinity Cycle



The depth at which CaCO3 dissolution exceeds supply (CCD) adjusts until the ocean sink for Alkalinity balances source.

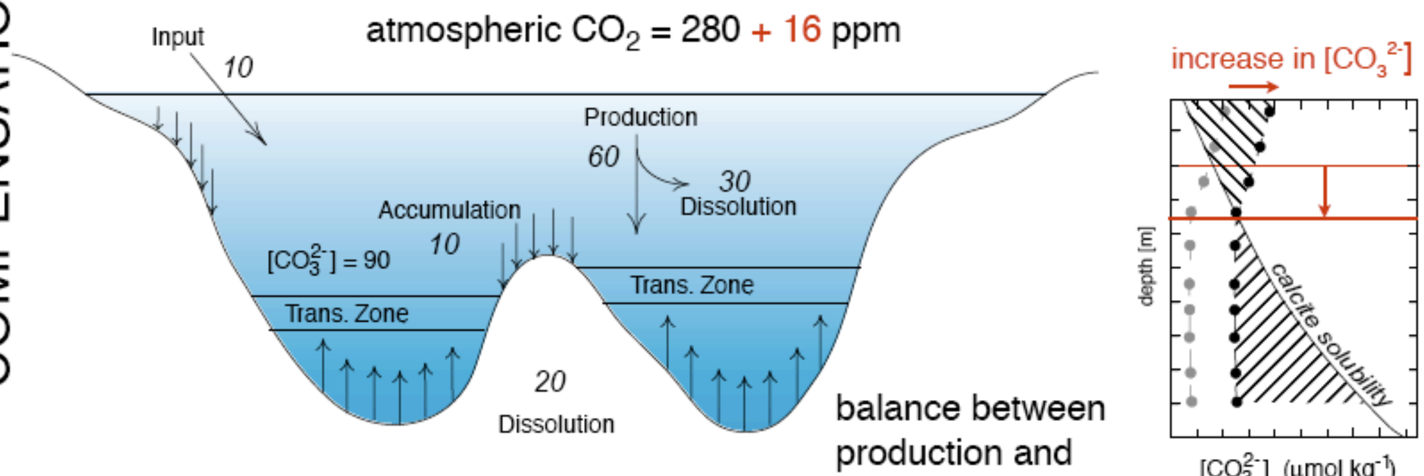
Addition of terrestrial carbon

PERTURBATION



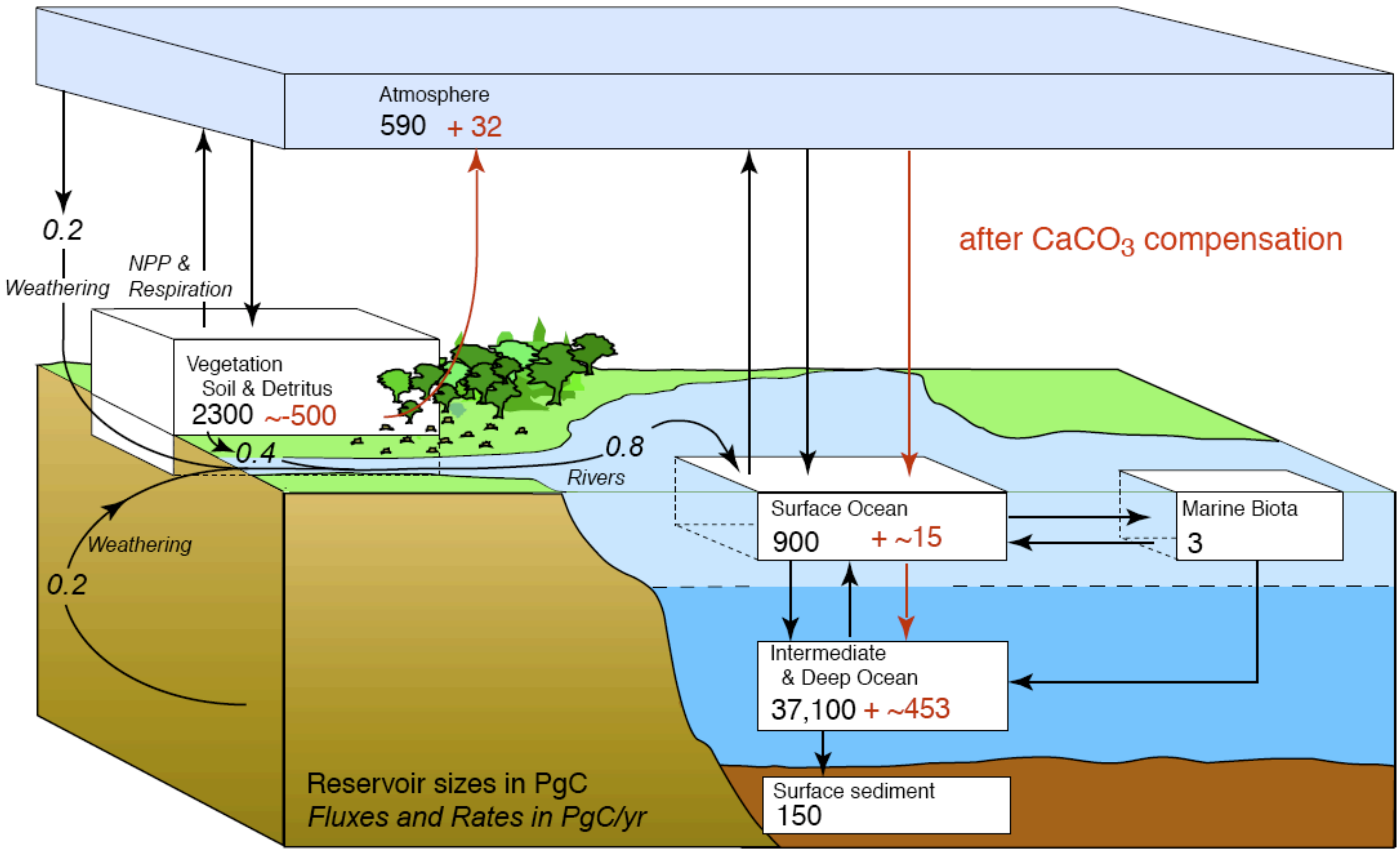
imbalance between production and deposition leads to extra dissolution and hence a slow increase in alkalinity that starts to compensate the increae in DIC

AFTER COMPENSATION



balance between production and deposition re-established

THE GLOBAL CARBON CYCLE AND ITS GLACIAL PERTURBATION



Influences on pCO_2

$$\boxed{pCO_2 \approx \frac{K_2}{K_0\, K_1} \frac{(2 \cdot DIC - Alk)^2}{Alk - DIC}}$$

‘solubility pump’

Changes in T, S of glacial ocean

‘organic carbon pump’

Changes in nutrient amount Or degree of high latitude nutrient consumption

‘calcium carbonate pump’

Changes in total alkalinity or its vertical gradient via plankton C_{org}:$CaCO_3$ ratio (the ‘rain ratio’)

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Changes in T, S
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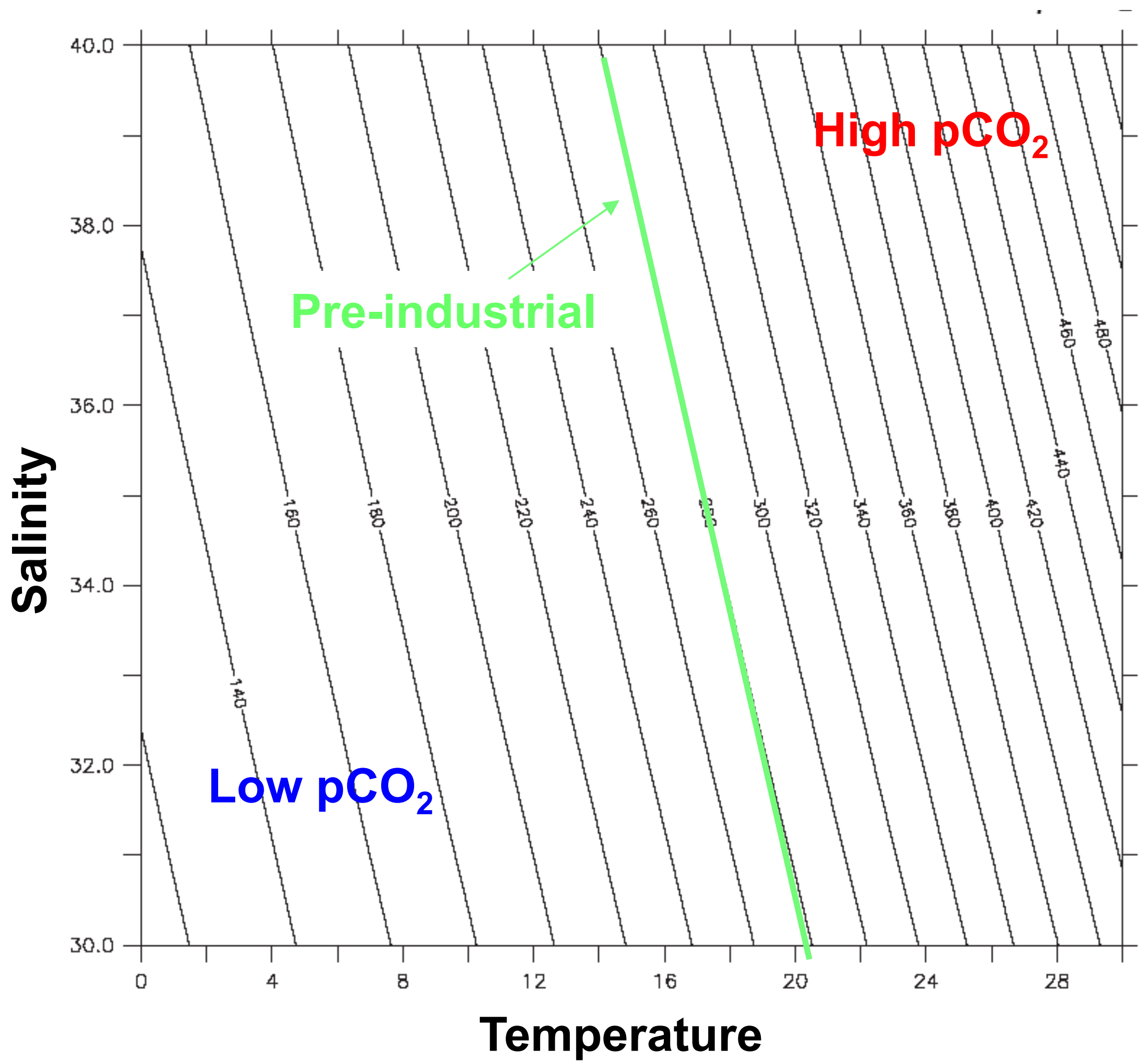
pCO_2 vs Temperature, Salinity



Sensitivity of pCO_2 to change in temperature

$\%\Delta pCO_2 \sim 4\%$ / deg C

Sensitivity of pCO_2 to change in Salinity

$\%\Delta pCO_2 / \%\Delta S \sim 1$

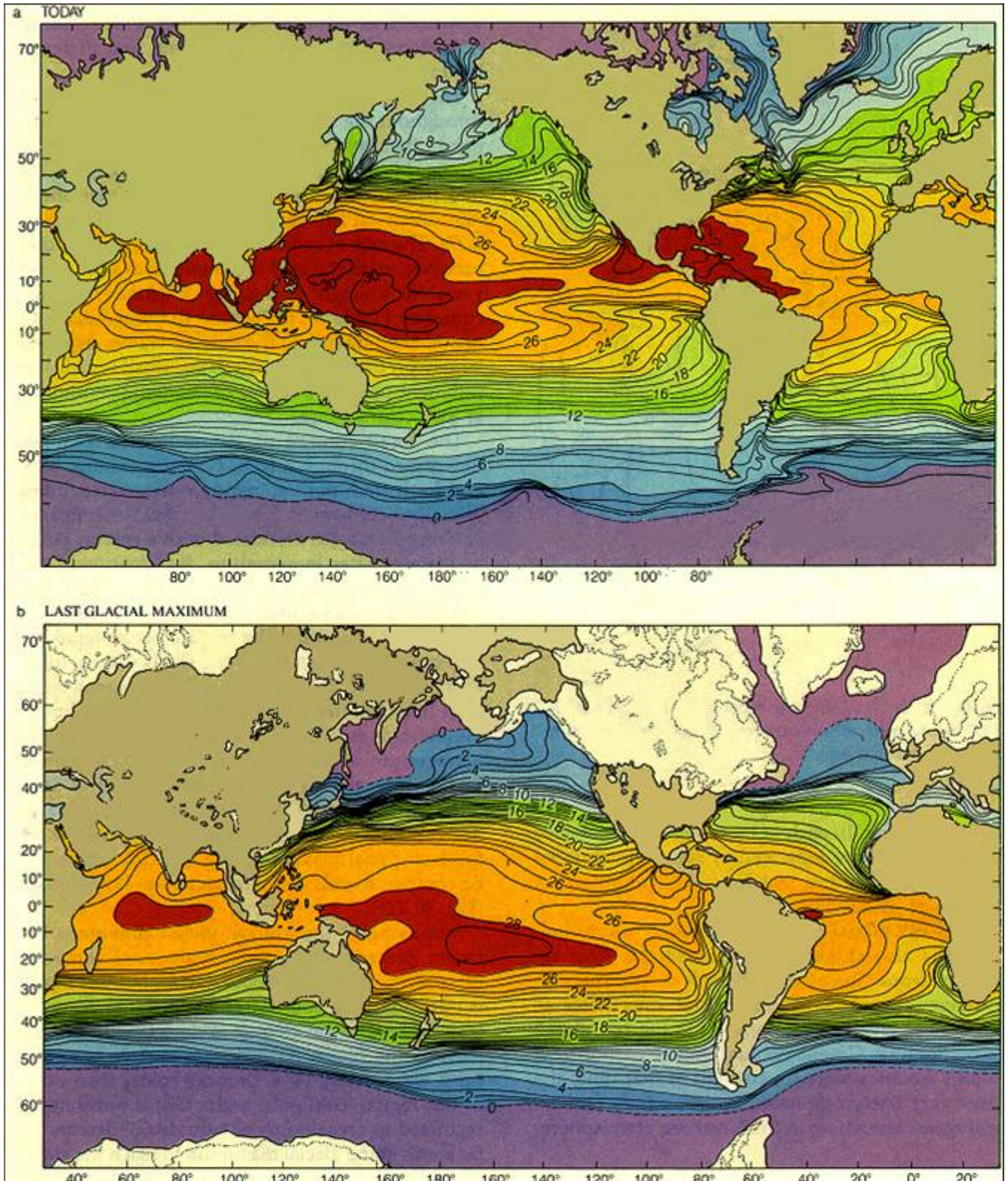


FIGURE 20.22 (*a*) Map showing modern sea-surface temperatures (°C) during August. (*b*) Map showing reconstructed August sea-surface temperatures during the last glacial maximum, about 18,000 years ago. Cold polar water extended far south of its present limit in the North Atlantic, and plumes of cold water flowed westward in the equatorial Pacific and Atlantic. (*Source:* After CLIMAP Project Members, 1976.)

Glacial Ocean Temperature and Salinity

Temperature estimates:

0-6 degrees colder in tropics
4 degrees colder (at most!) in polar ocean
---> ~ 30 ppm lower pCO_2

Sea level ~120 m lower
Salinity ~ 3% higher
--> 7 ppm higher pCO_2

Three easy pieces

Table 1 Atmospheric CO_2 effects of known changes

Condition during the last ice age (as different from Holocene)	CO_2 change (p.p.m.v.)
Terrestrial carbon decrease (500 Pg C)	15
Ocean cooling (5° low latitude, 2.5° high latitude)	–30
Ocean salinity increase (3%)	6.5
Total CO_2 change	–8.5

Still a long way to go…

Sigman and Boyle [2001]

Influences on pCO_2

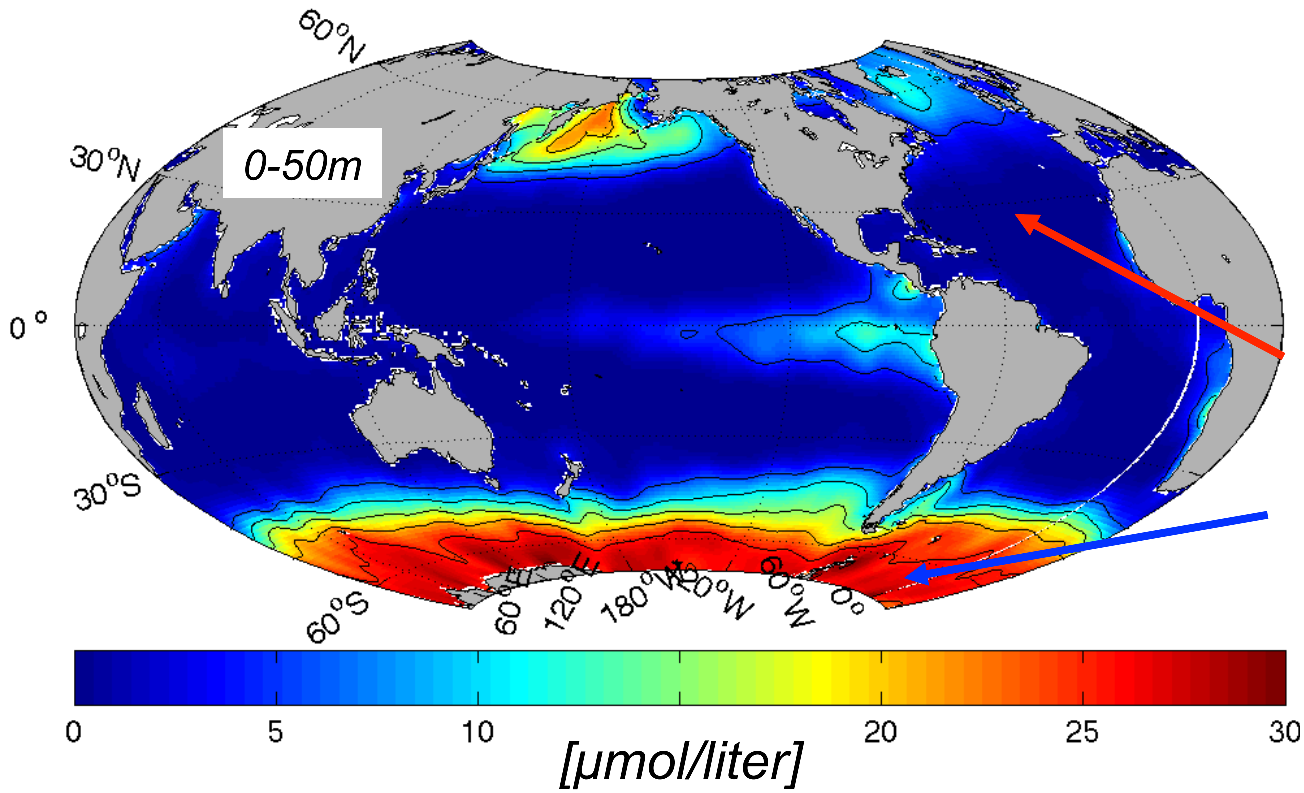
$$\boxed{pCO_2 \approx \frac{K_2}{K_0\,K_1}\frac{(2\cdot DIC - Alk)^2}{Alk - DIC}}$$

‘organic carbon pump’

Changes in nutrient amount
Or degree of high latitude
nutrient consumption

Biological CO_2 Storage

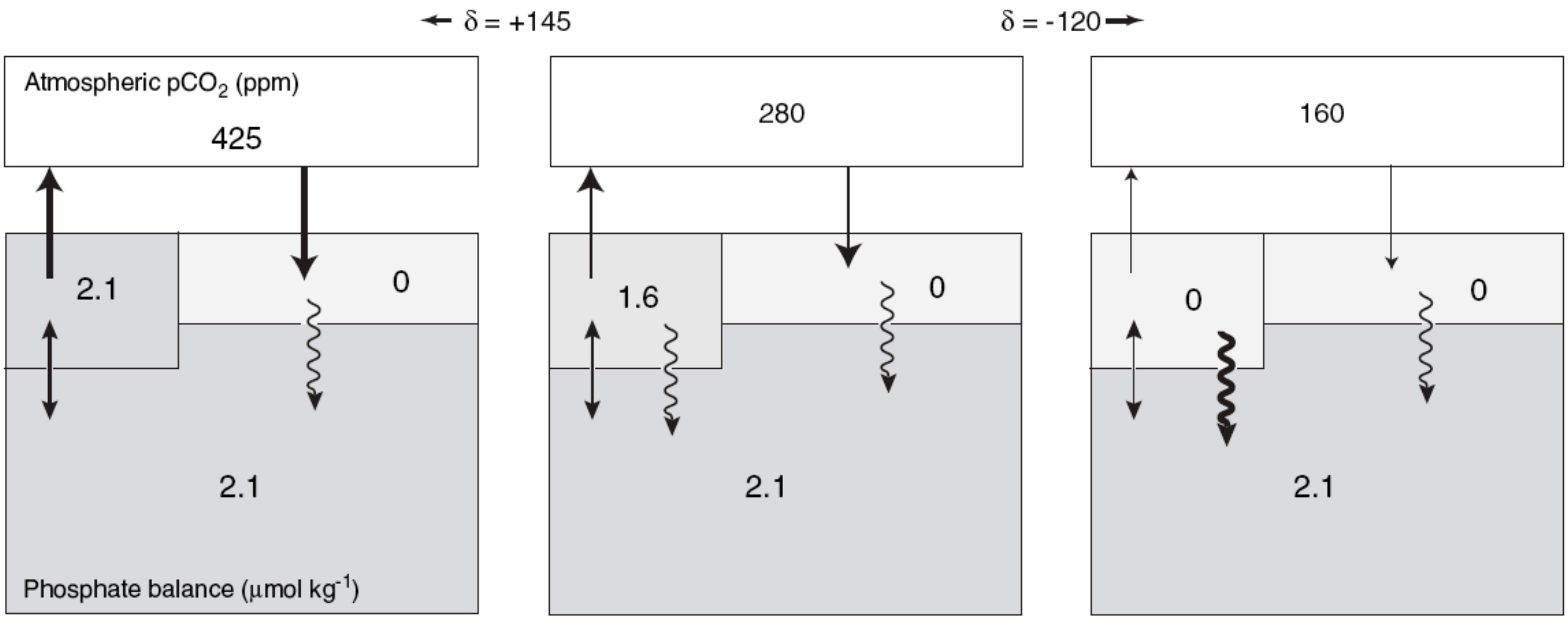
Annual mean surface $[NO_3^-]$



Changes in biological carbon storage can occur via changes in:

1) *Nutrient reservoir (low latitudes)*
2) *Nutrient utilization (high latitudes)*

High Latitude Sensitivity



Sarmiento and Toggweiler [1984], Knox and McElroy [1985], Siegenthaler and Wenk [1984]

But is this sensitivity model dependent?

Changing Carbon Storage

Perturbation: $$\cancel{\delta C} = \delta C_{atm} + \delta C_{reg} + \delta C_{pre} + \cancel{\delta C_{diseq}}$$

then $$\frac{\delta C_{atm}}{\delta C_{reg}} = \frac{1}{\phi}$$

Look familiar?
It's the same problem as before!
Why?

Nutrient stoichiometry
And conservation

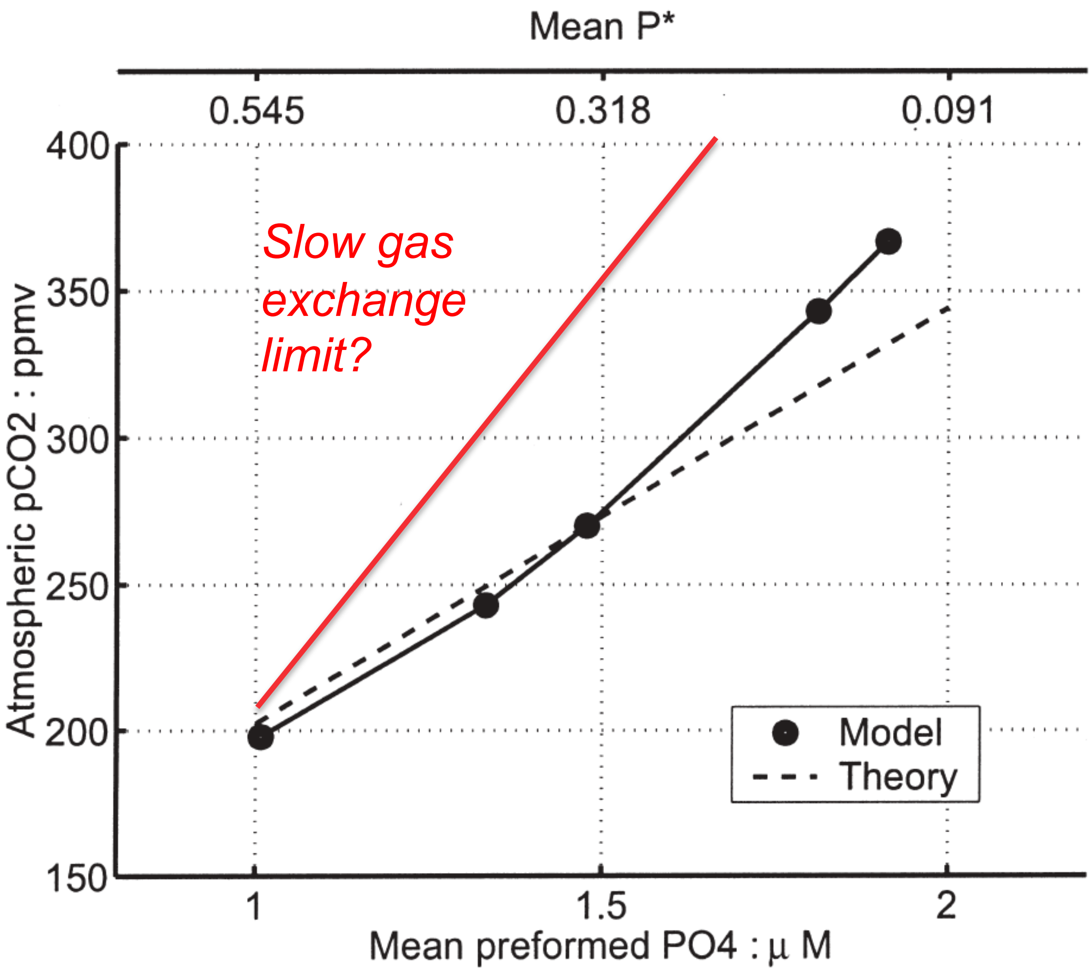
$$\delta C_{reg} = R_{C:P}\delta P_{reg} = -R_{C:P}\delta P_{pre}$$

Note: These are volume
weighted means!

$$P_{pre} = \sum_{Xo} P(x_0) \cdot V(x_0)$$

Ito and Follows [2005]

Fast gas exchange limit



GCM experiments forcing surface nutrients toward zero, with high piston velocity.

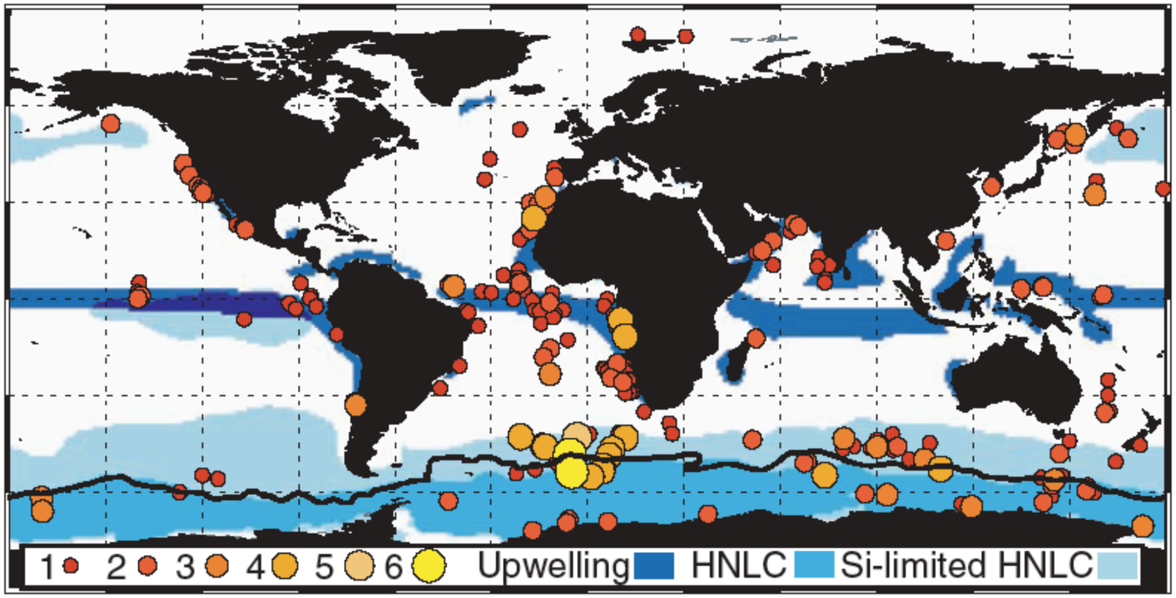
Recall colloquium presentation by Taka Ito:

High latitudes have slow gas exchange because of deep mixed layers and small surface residence time.

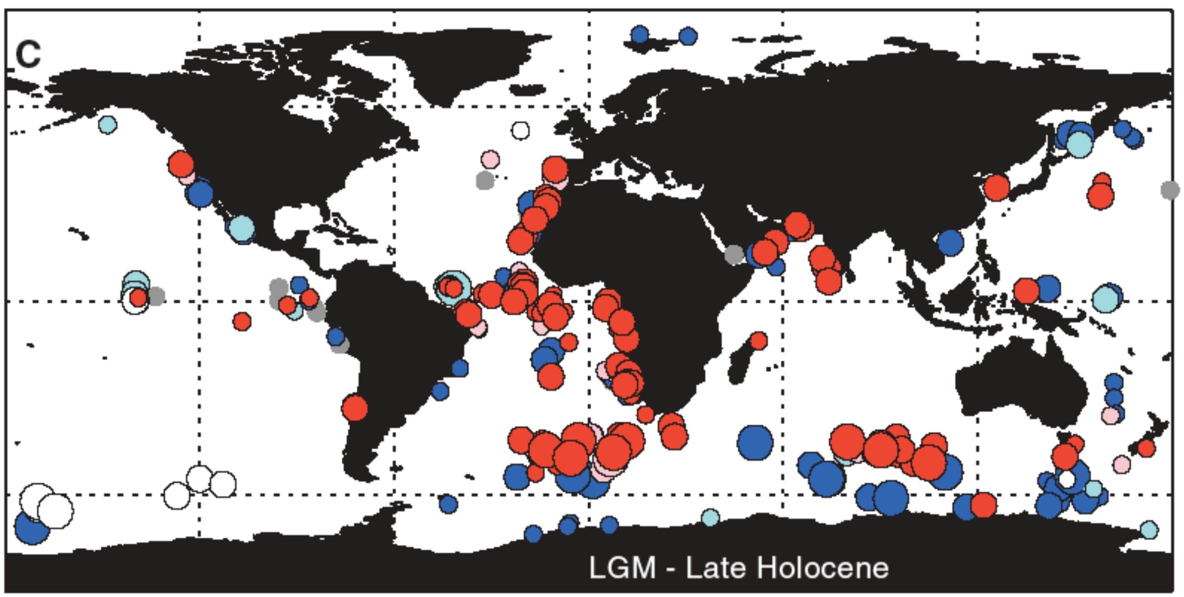
In slow gas exchange limit, increased storage can be enhanced by ~50%.

Ito and Follows [2005]

Glacial Productivity



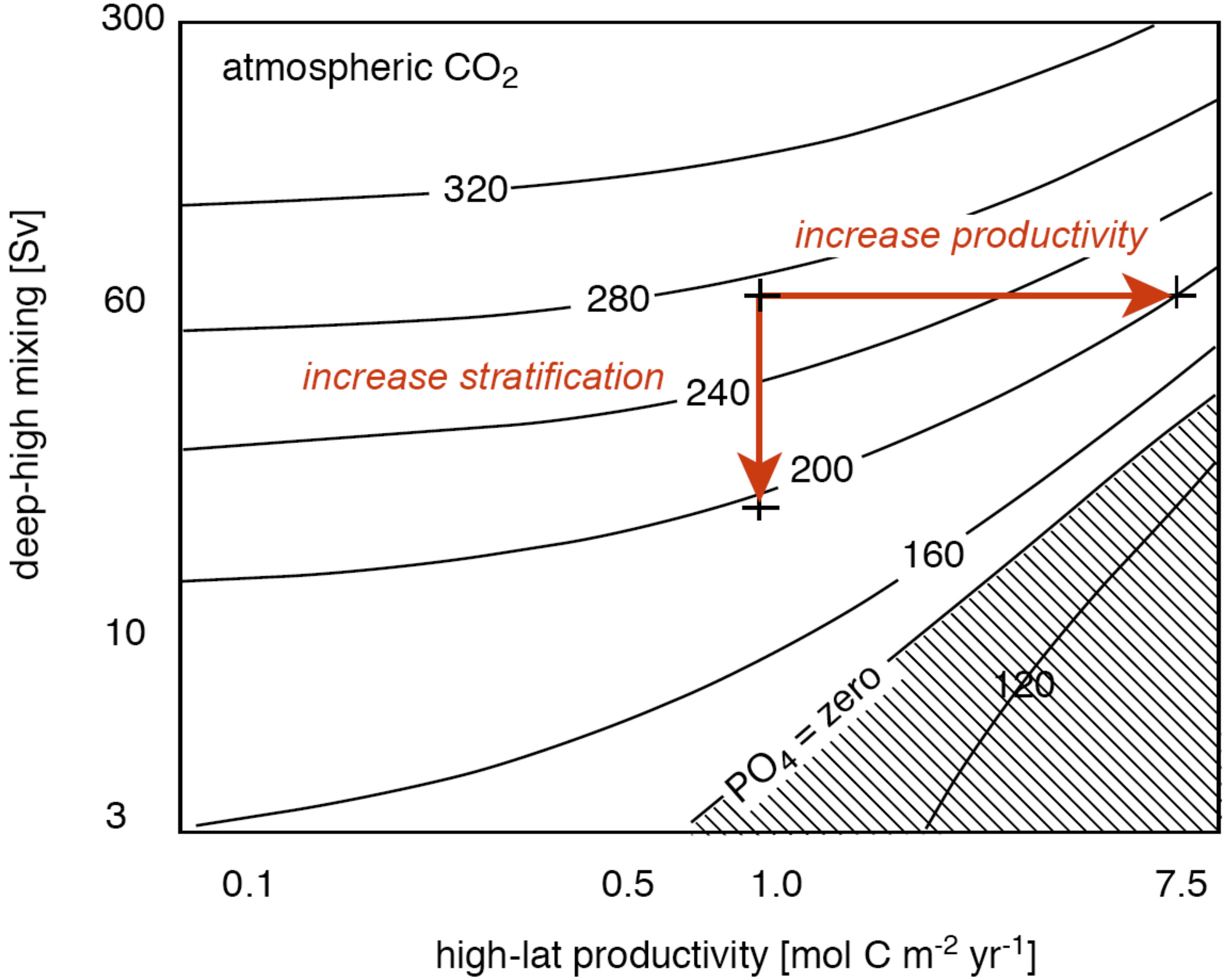
Assembly of multiple proxies in the sediment record for changes in export flux provides the most robust evaluation.



Low latitudes generally imply larger export during ice age. So does the Subantarctic. The Antarctic seems to have the opposite change.

Kohfeld et al. [2005]

Two paths to efficiency

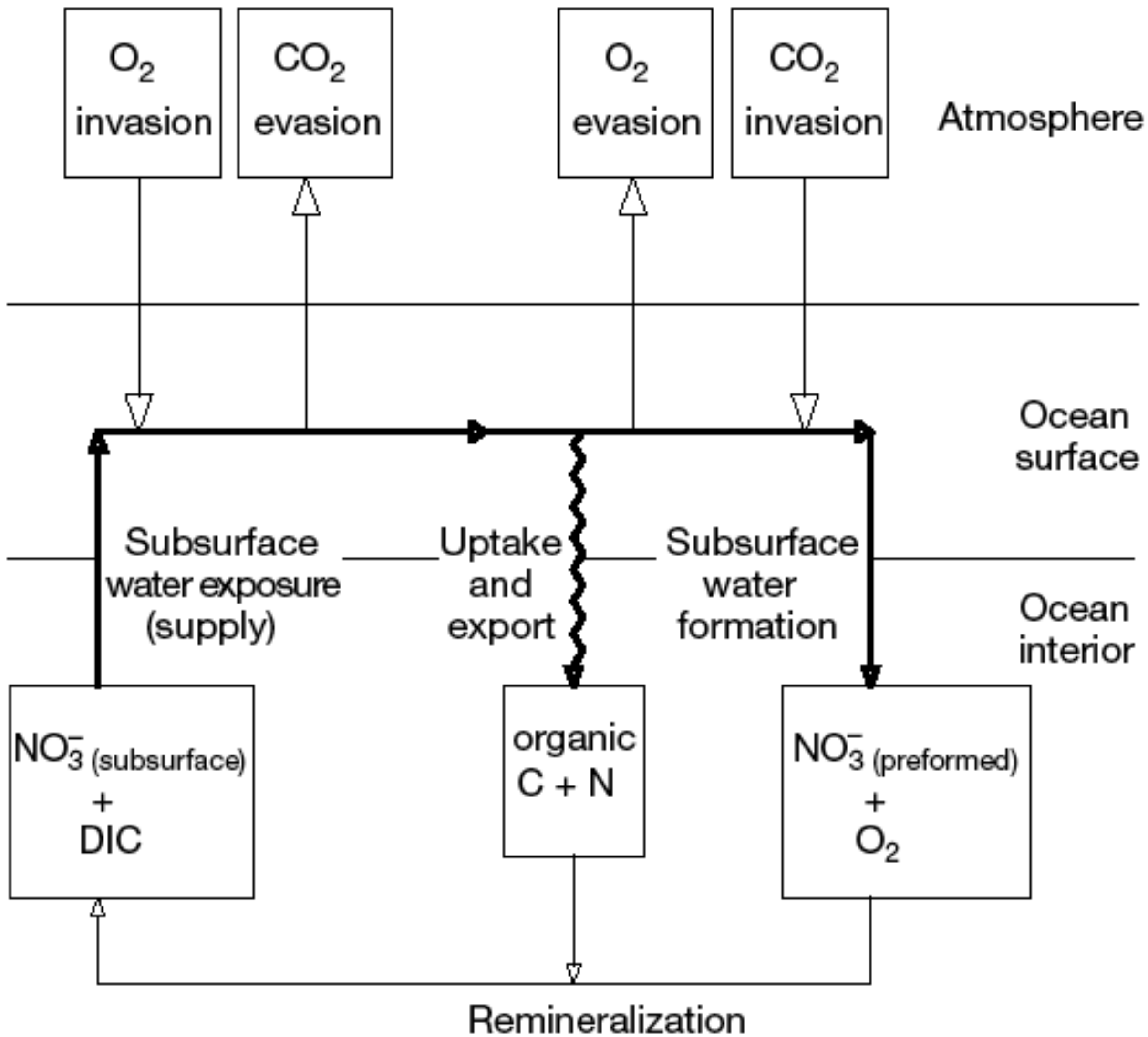


Can draw down pCO2 by either:

1) increased export or
2) reduced vertical exchange

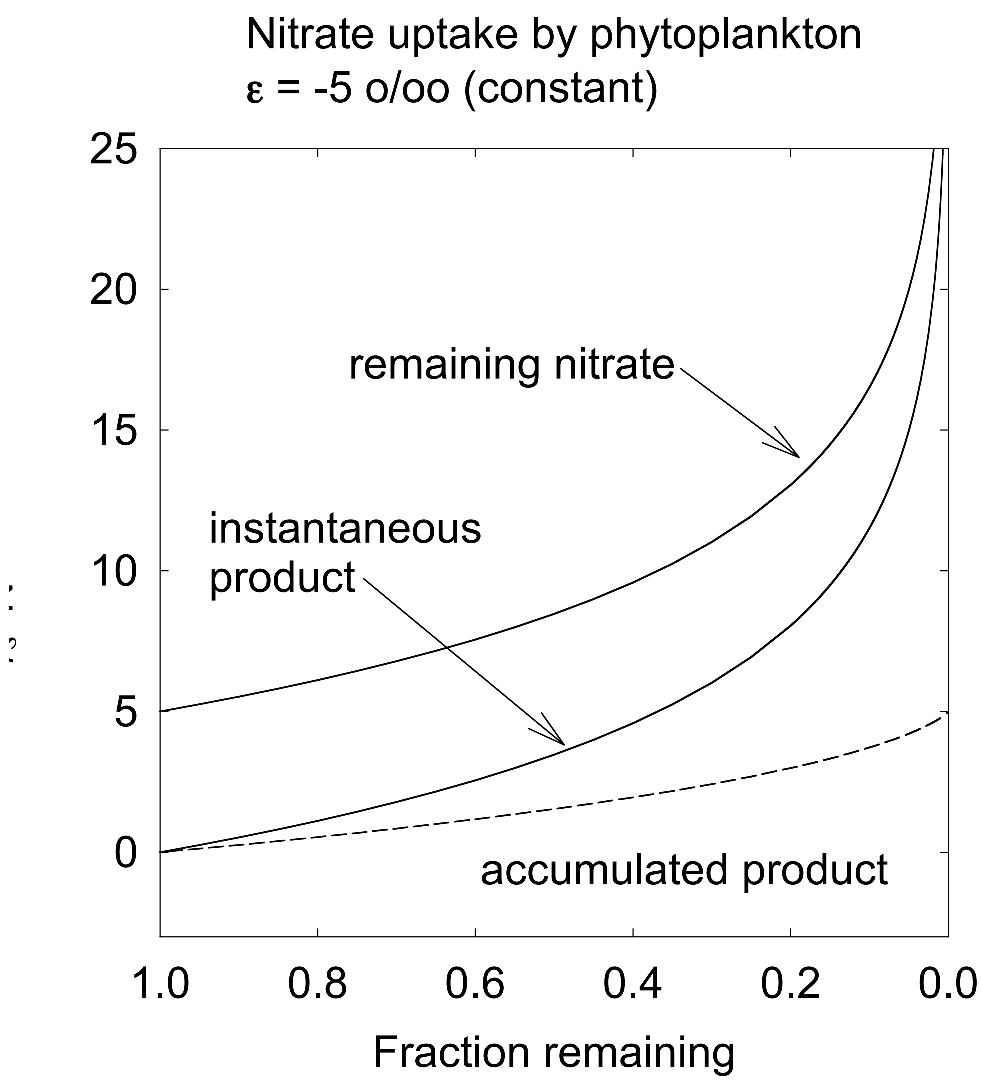
An increase in export alone is not necessary or sufficient to reduce pCO2.

Utilization as a metric for efficiency



$$\text{Nutrient utilization} \equiv \frac{\text{Uptake}}{\text{Supply}} = 1 - \frac{[NO_3^-]_{\text{preformed}}}{[NO_3^-]_{\text{subsurface}}} \propto \frac{CO_2 \ \text{invasion}}{CO_2 \ \text{evasion}}$$

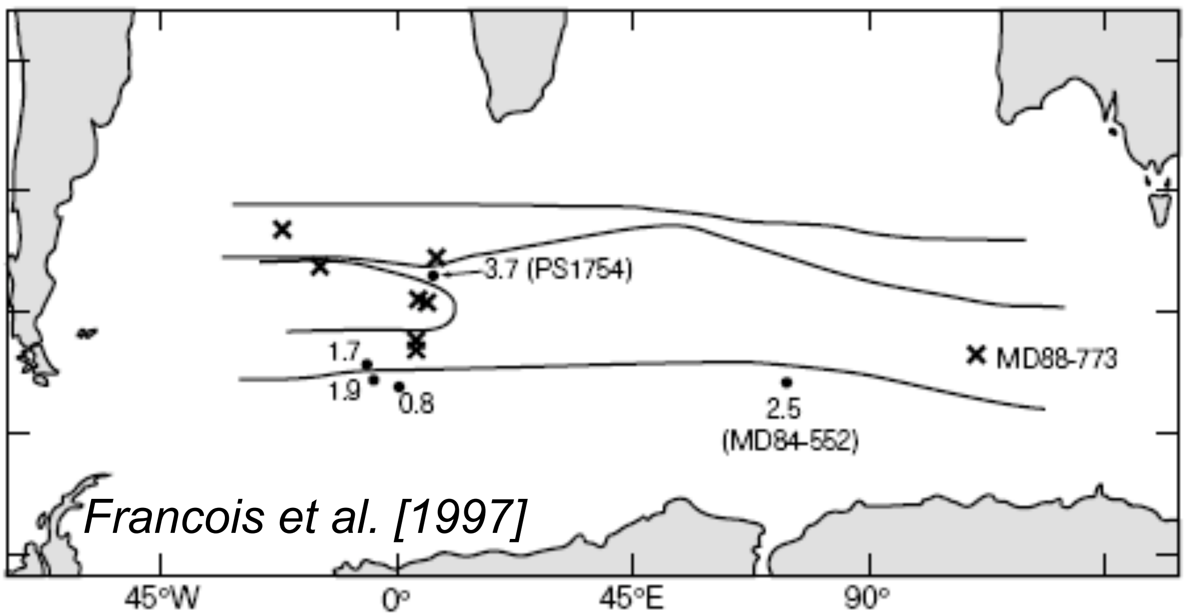
Fractional nutrient utilization

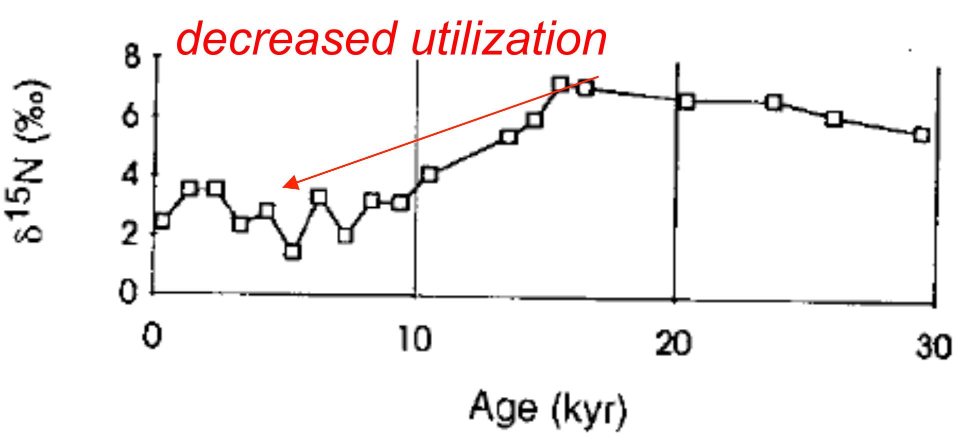


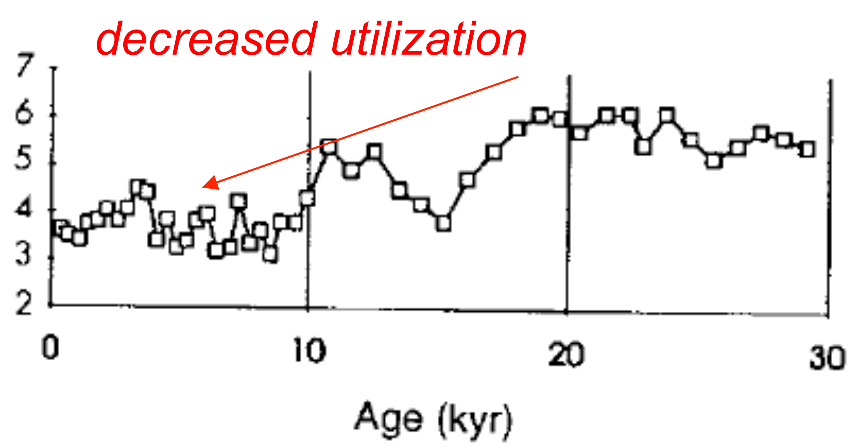
Rayleigh-type fractionation as a model of nitrate uptake during photosynthesis.

As utilization of the reactant nears completion, the accumulated product (integrated product) approaches the isotopic composition of the initial reactant.

Glacial nutrient utilization



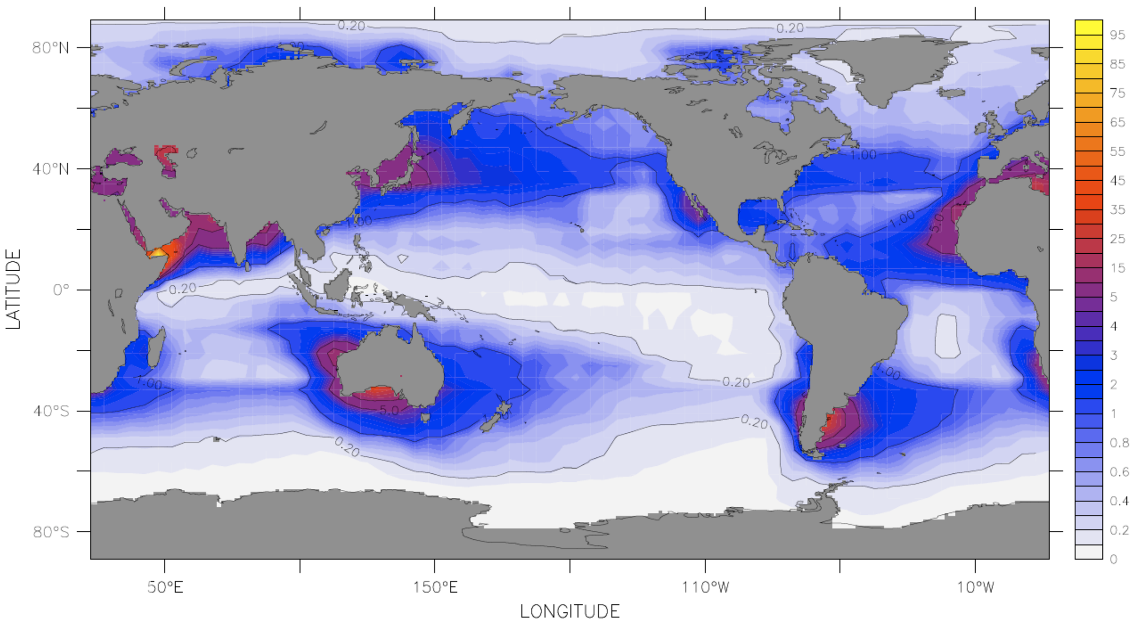


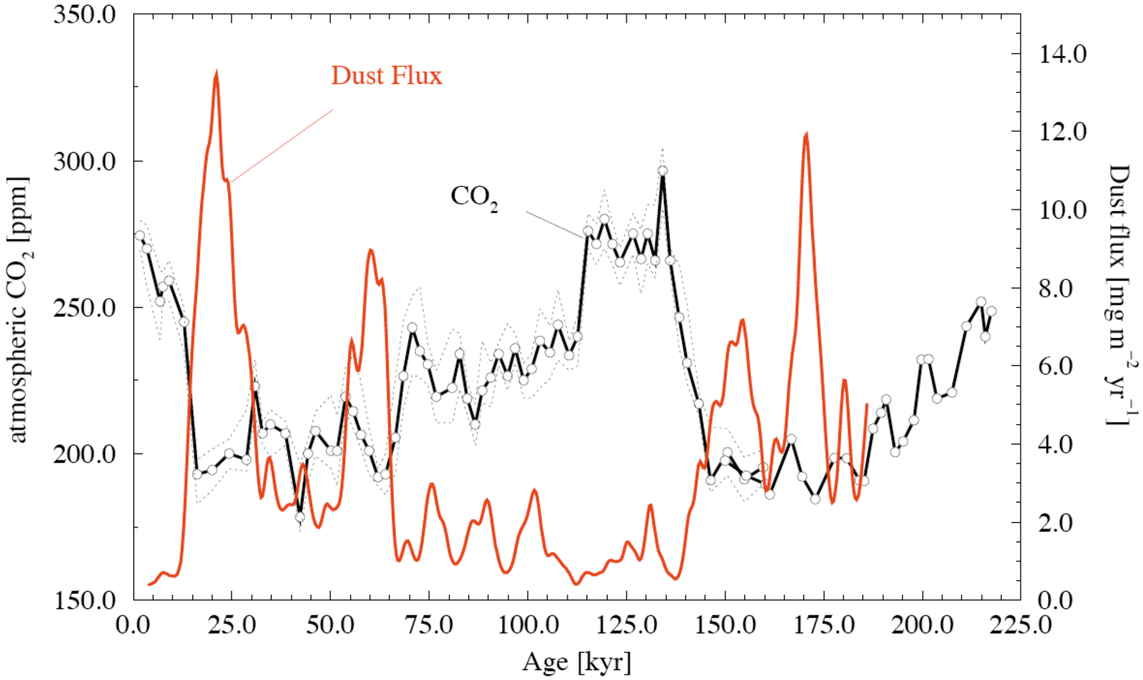


Causes of higher glacial N utilization:

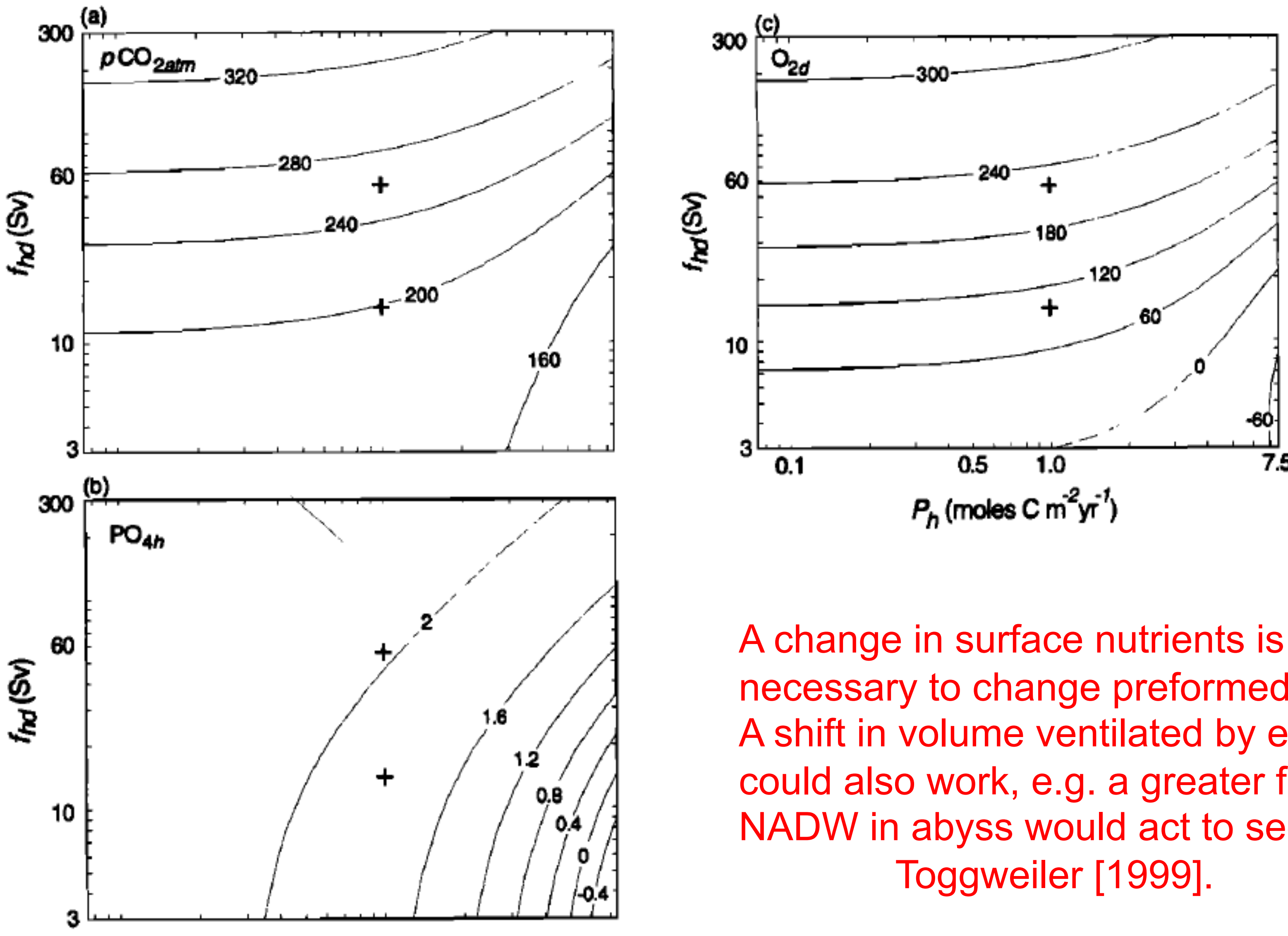
1) Dust deposition

Dust deposition over the ocean [*Tegen and Fung*, 1997]





Constant nutrients, changing pCO_2?

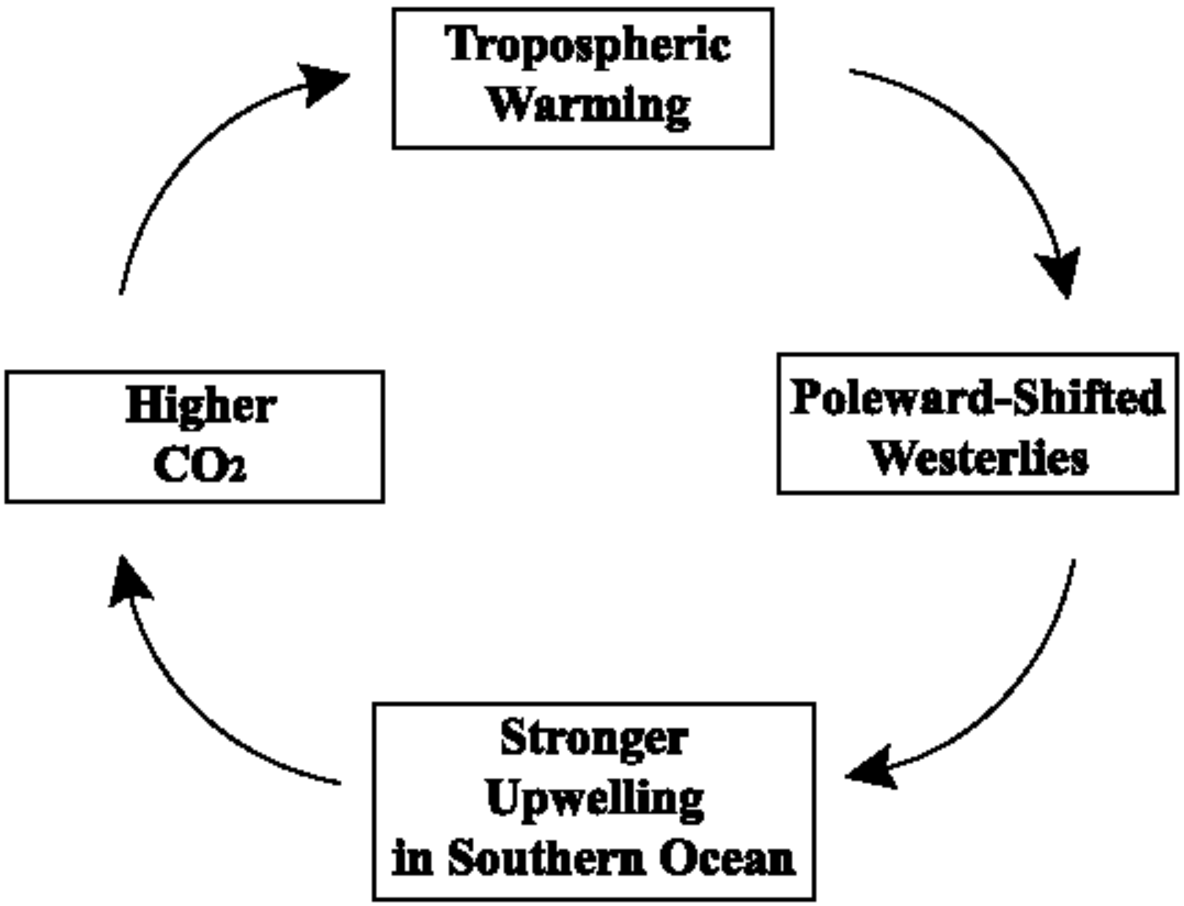


A change in surface nutrients is not necessary to change preformed nutrients! A shift in volume ventilated by each region could also work, e.g. a greater fraction of NADW in abyss would act to sequester C.

Toggweiler [1999].

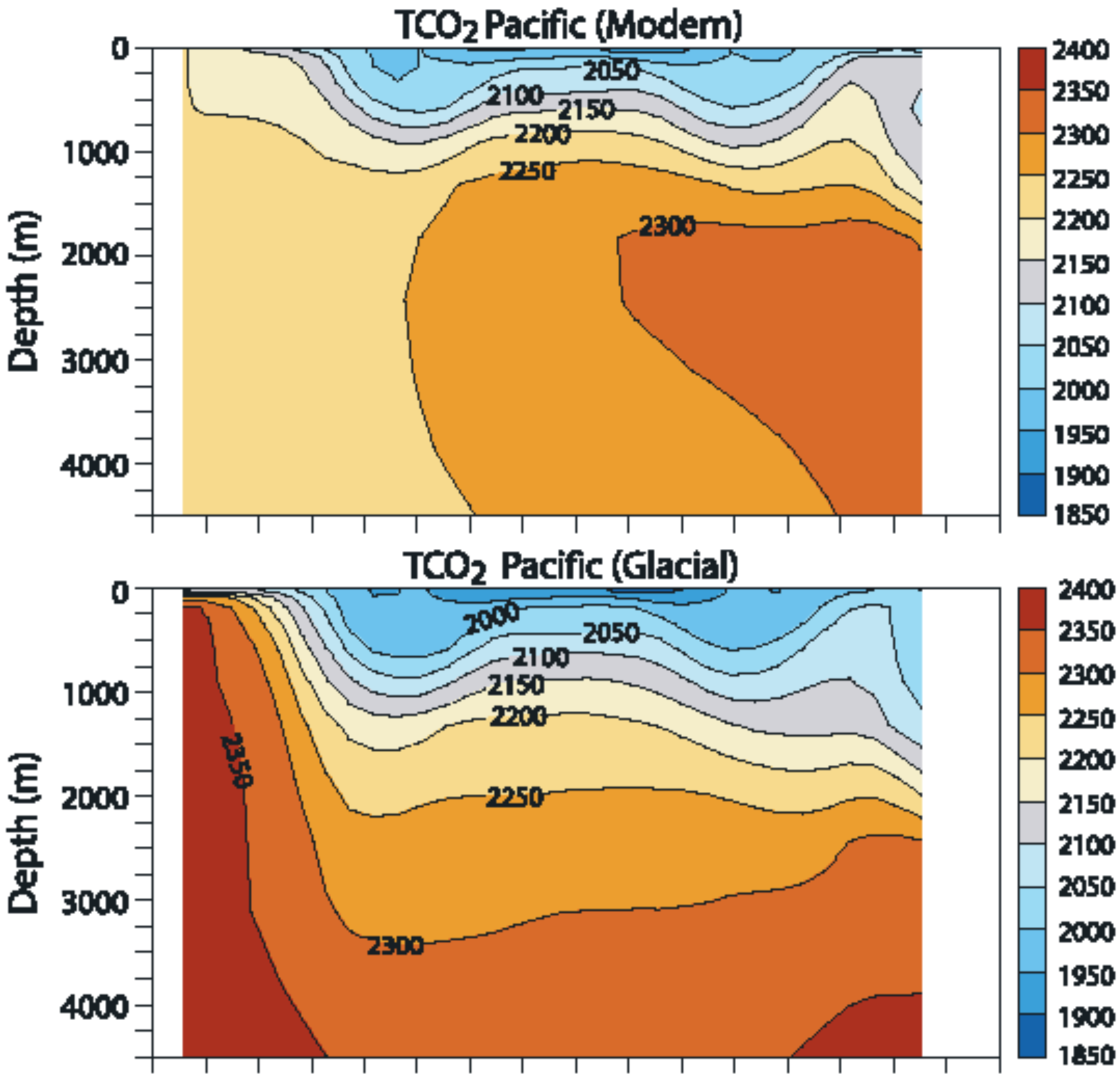
Causes of higher glacial N utilization:

2) Circulation



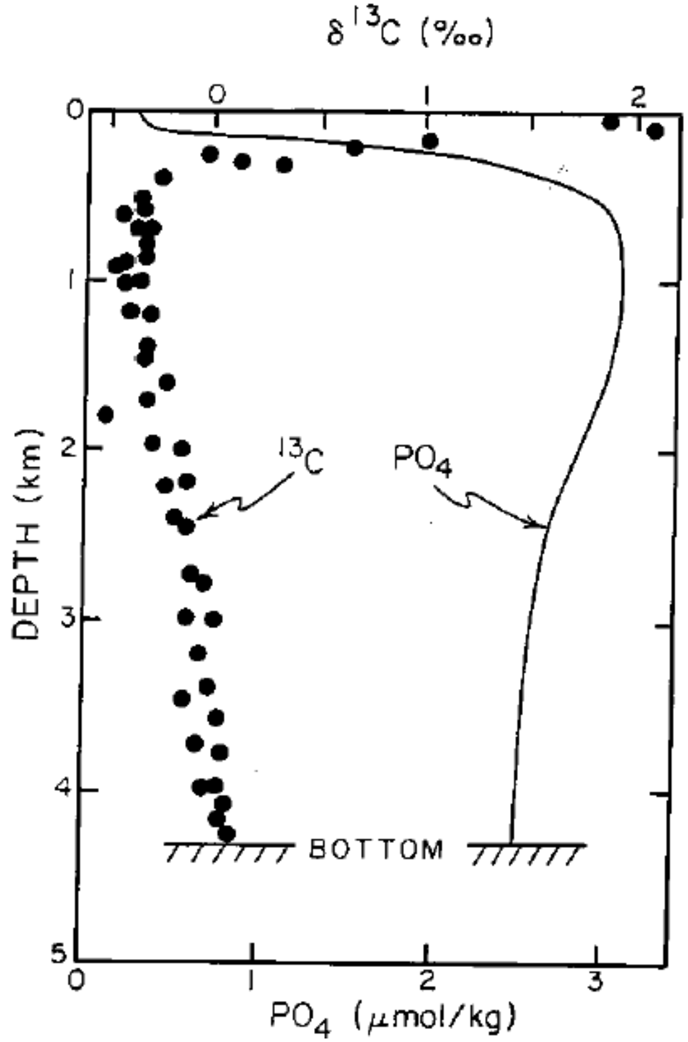
Toggweiler et al. [2006]

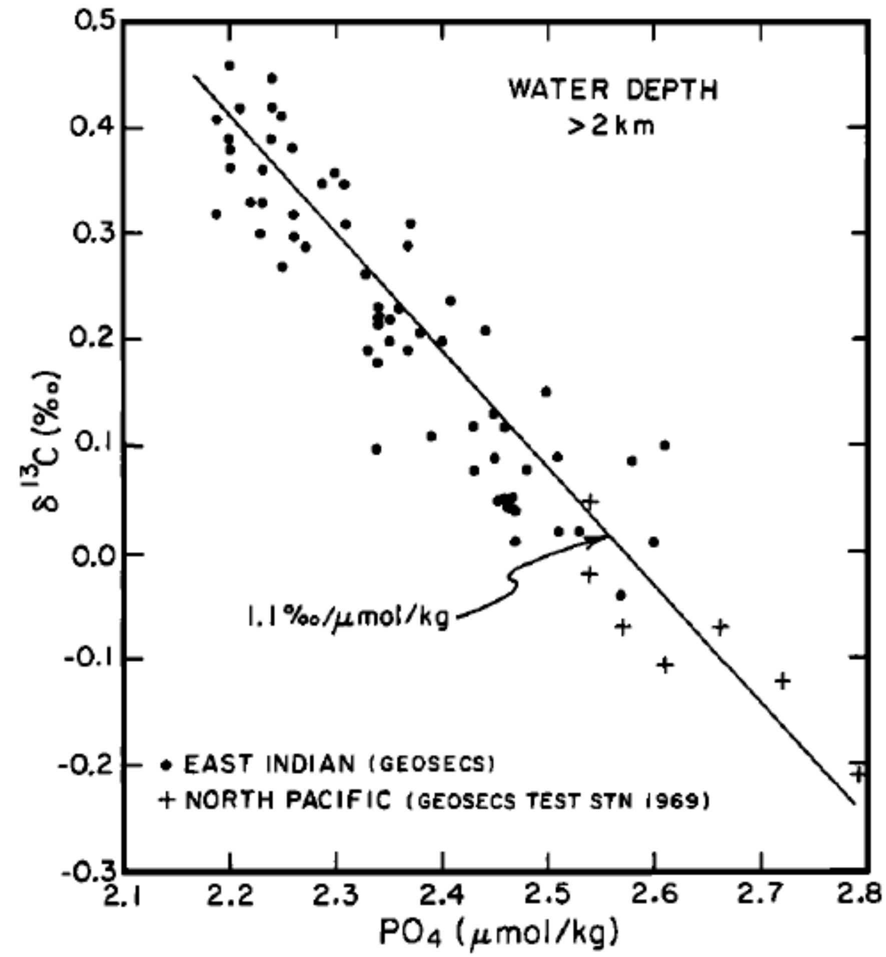
Consequences of higher glacial N utilization:



Toggweiler et al. [2006]

Water mass tracer: $\delta^{13}C$

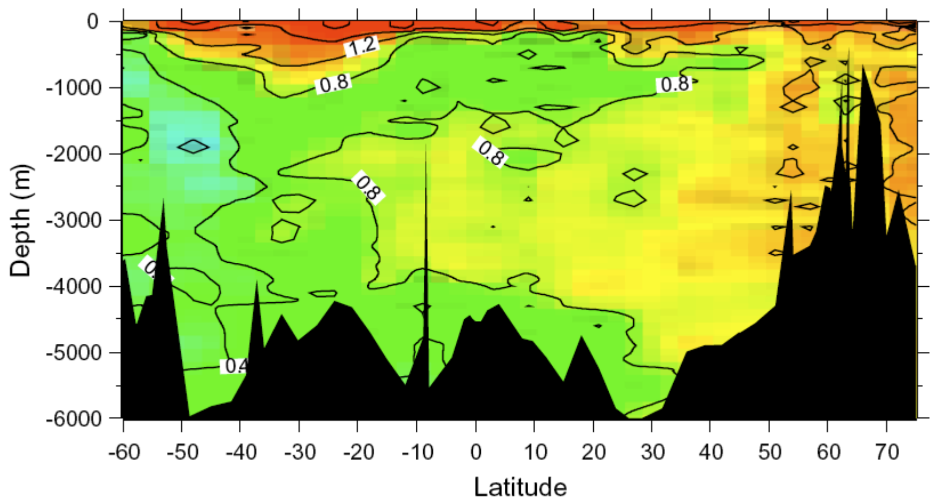




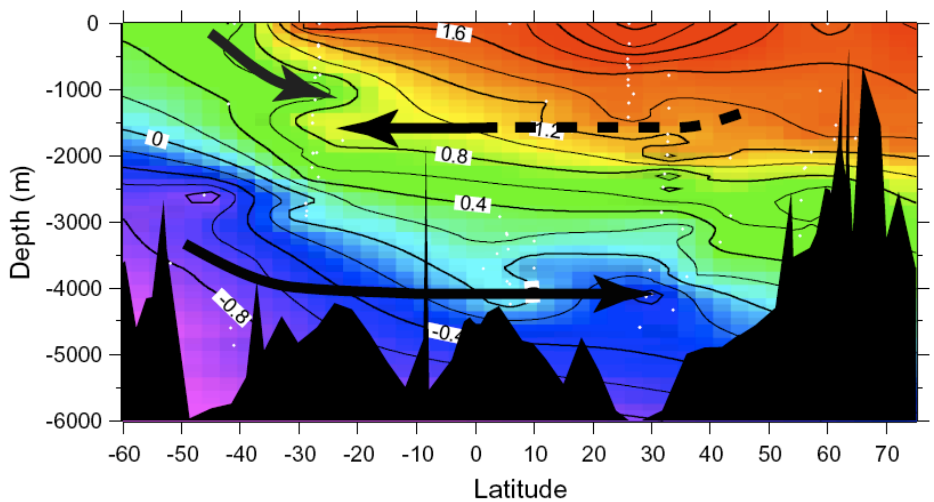
Phosphate and $\delta^{13}C$ of DIC in the Pacific Ocean [Broecker and Peng, 1982]. The $\delta^{13}C$ of DIC is a mirror image of PO_4 because photosynthesis preferentially ^{12}C faster than ^{13}C.

Glacial Deep Atlantic

Western Atlantic GEOSECS $\delta^{13}C$ (PDB)



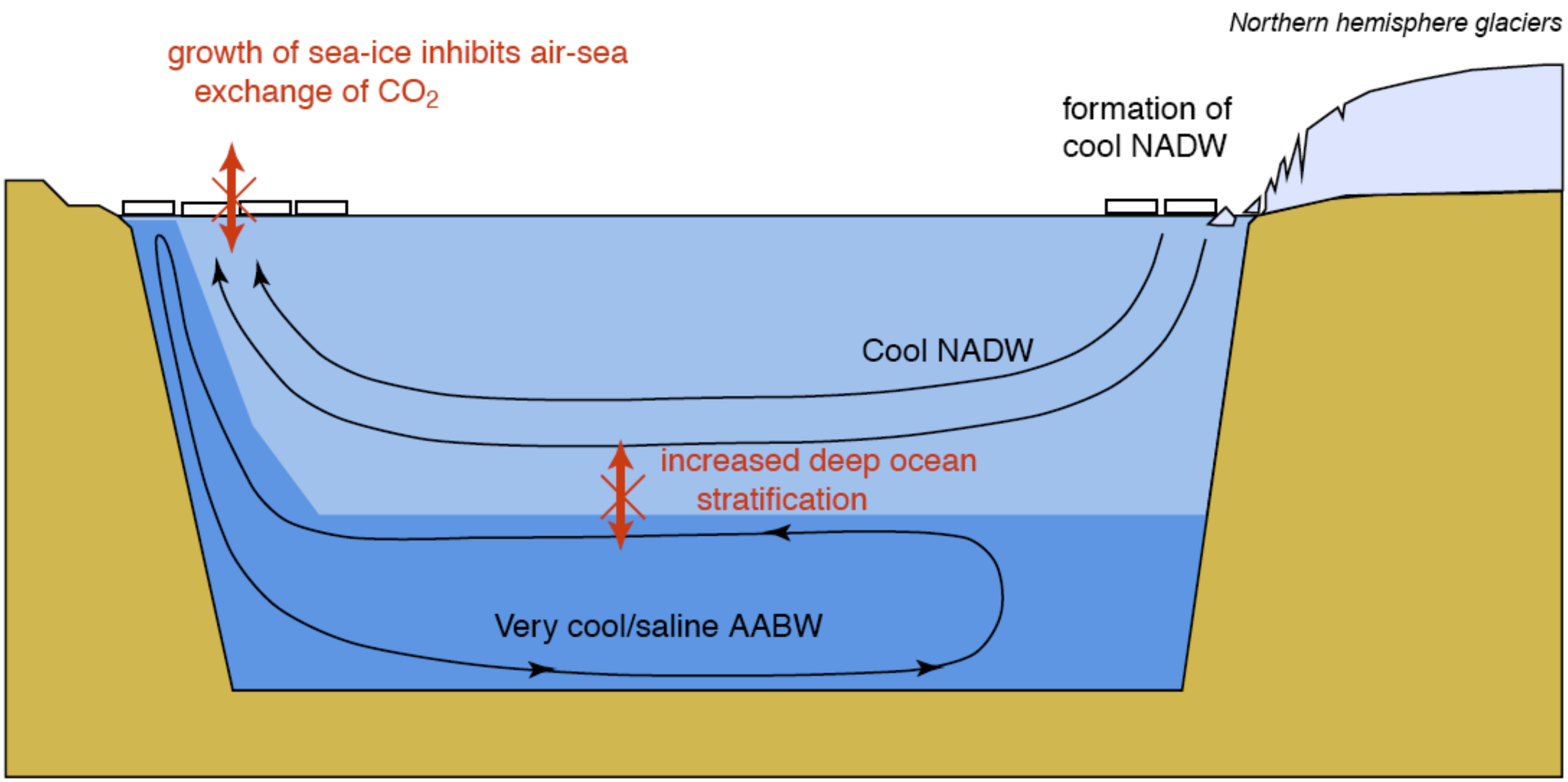
Western Atlantic Glacial $\delta^{13}C$ (PDB)



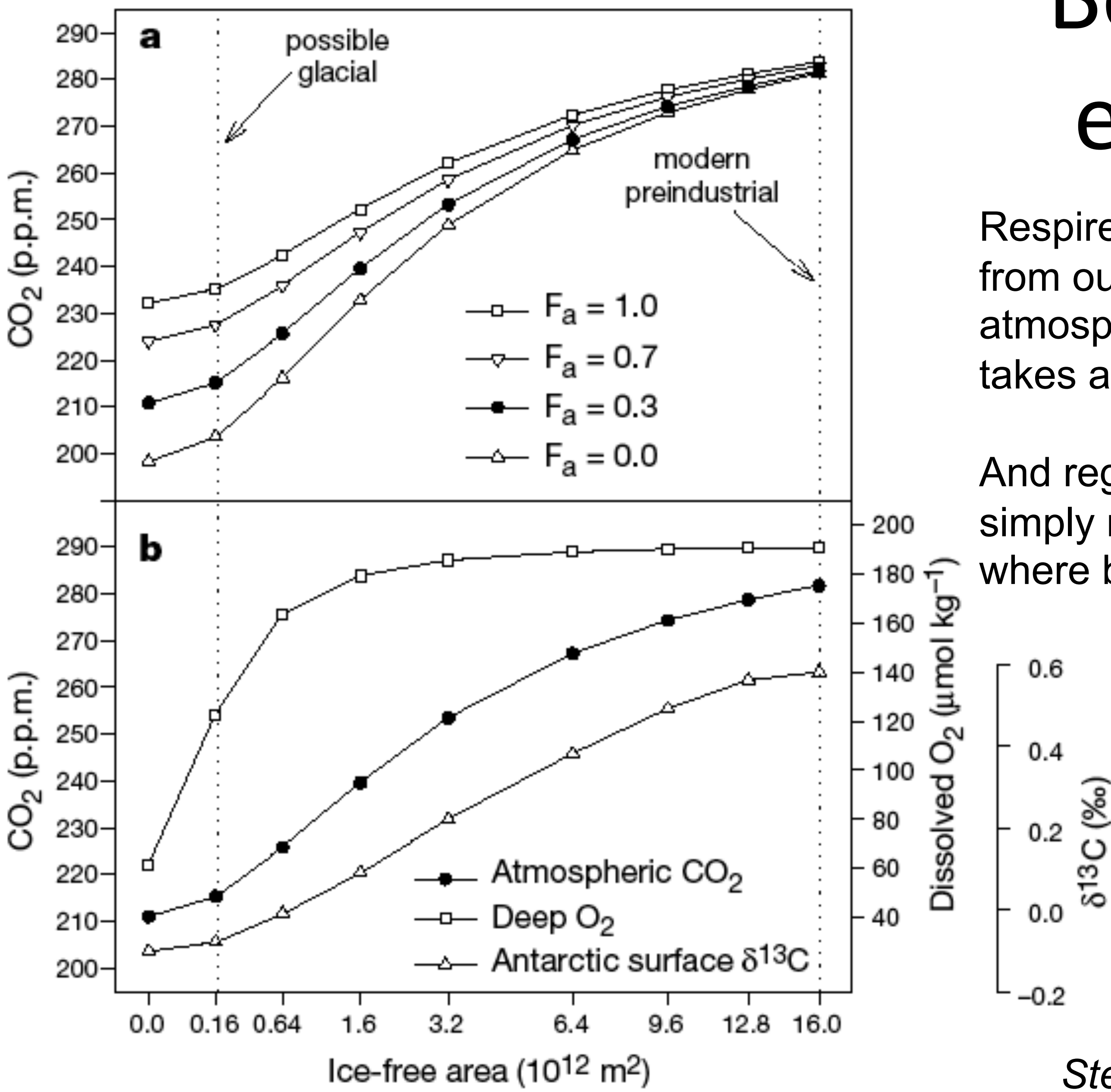
Modern and glacial $\delta^{13}C$ distributions from the Western Atlantic. Glacial values are reconstructed from multiple sediment cores (small white dots). Interpretation: low-nutrient NADW was much shallower and high nutrient AABW was more extensive than now.

Curry and Oppo [2005]

Sea Ice - Blocking the exit



Box model estimates



Respired DIC can be prevented from outgassing to the atmosphere by sea ice, but it takes a lot of ice to do it.

And regions of convection may simply move to open areas where buoyancy loss can occur?

Stephens and Keeling [2000]

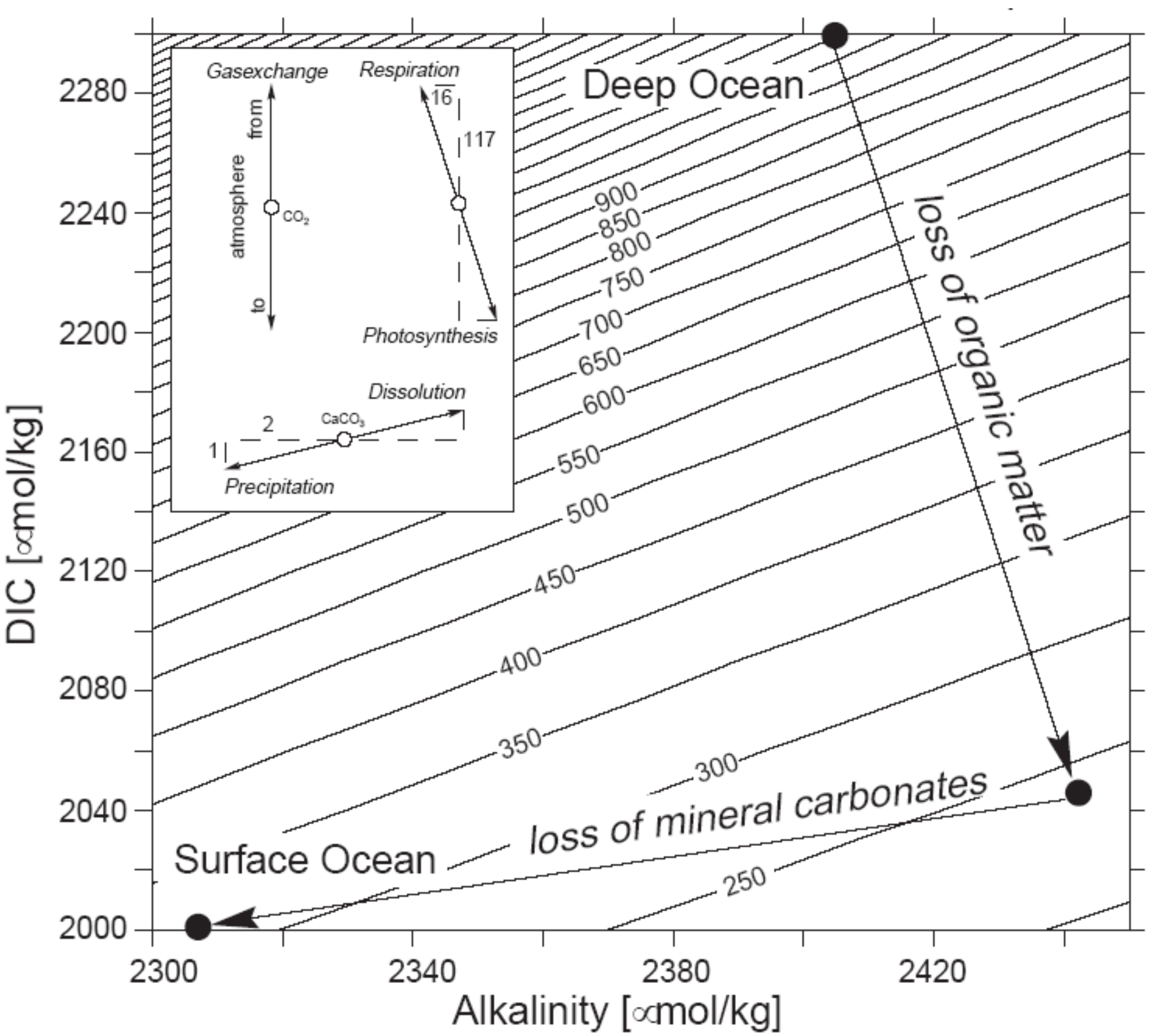
Influences on pCO_2

$$\boxed{pCO_2 \approx \frac{K_2}{K_0\,K_1}\frac{(2\cdot DIC - Alk)^2}{Alk - DIC}}$$

‘calcium carbonate pump’

Changes in total alkalinity or its vertical gradient via plankton C_{org}:$CaCO_3$ ratio (the ‘rain ratio’)

Carbonate pump and pCO_2



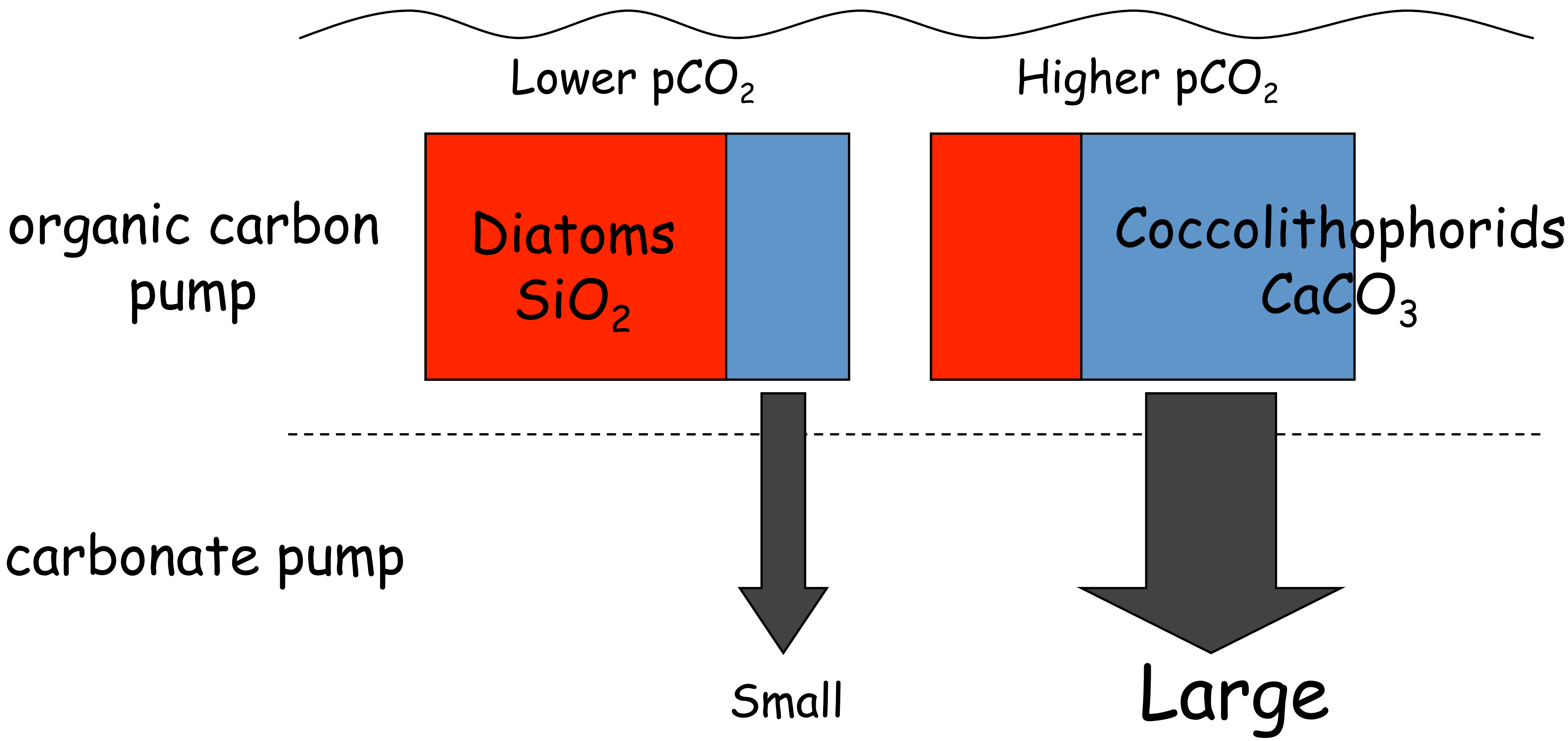
Sarmiento and Gruber [2006]

Current estimates are that ~10% of carbon export is in the form of CaCO3.

This fraction is referred to as the rain ratio.

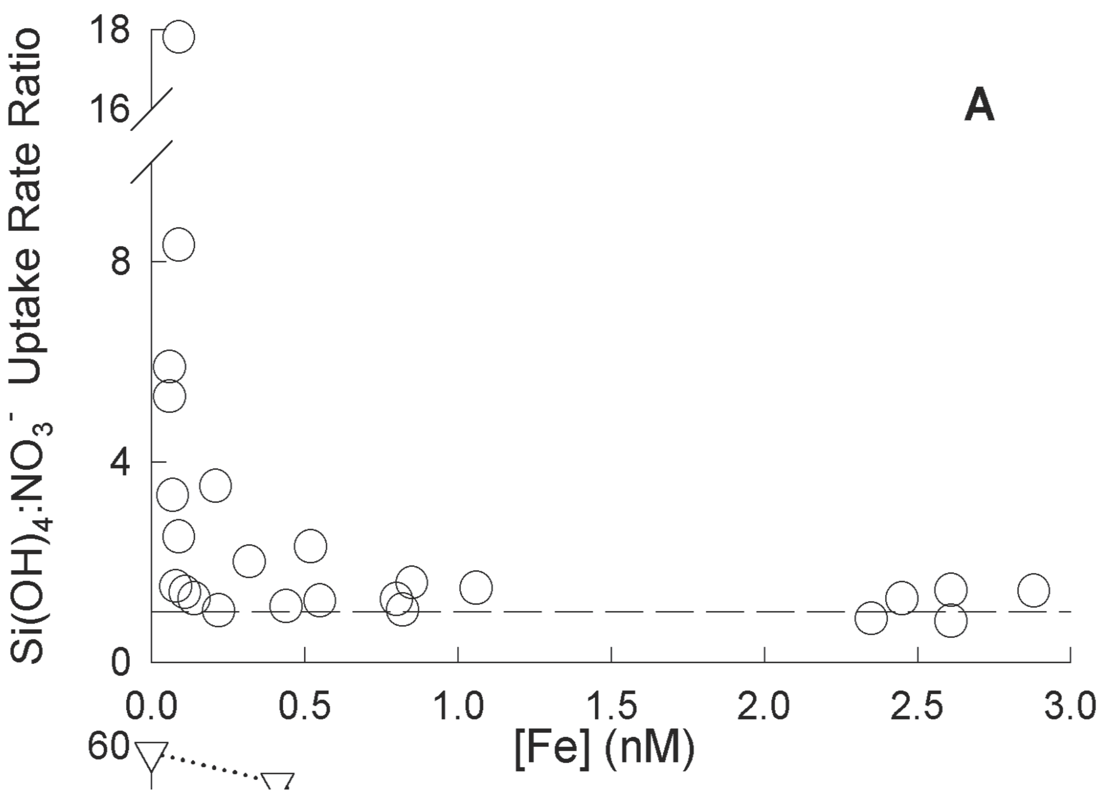
Rain Ratio

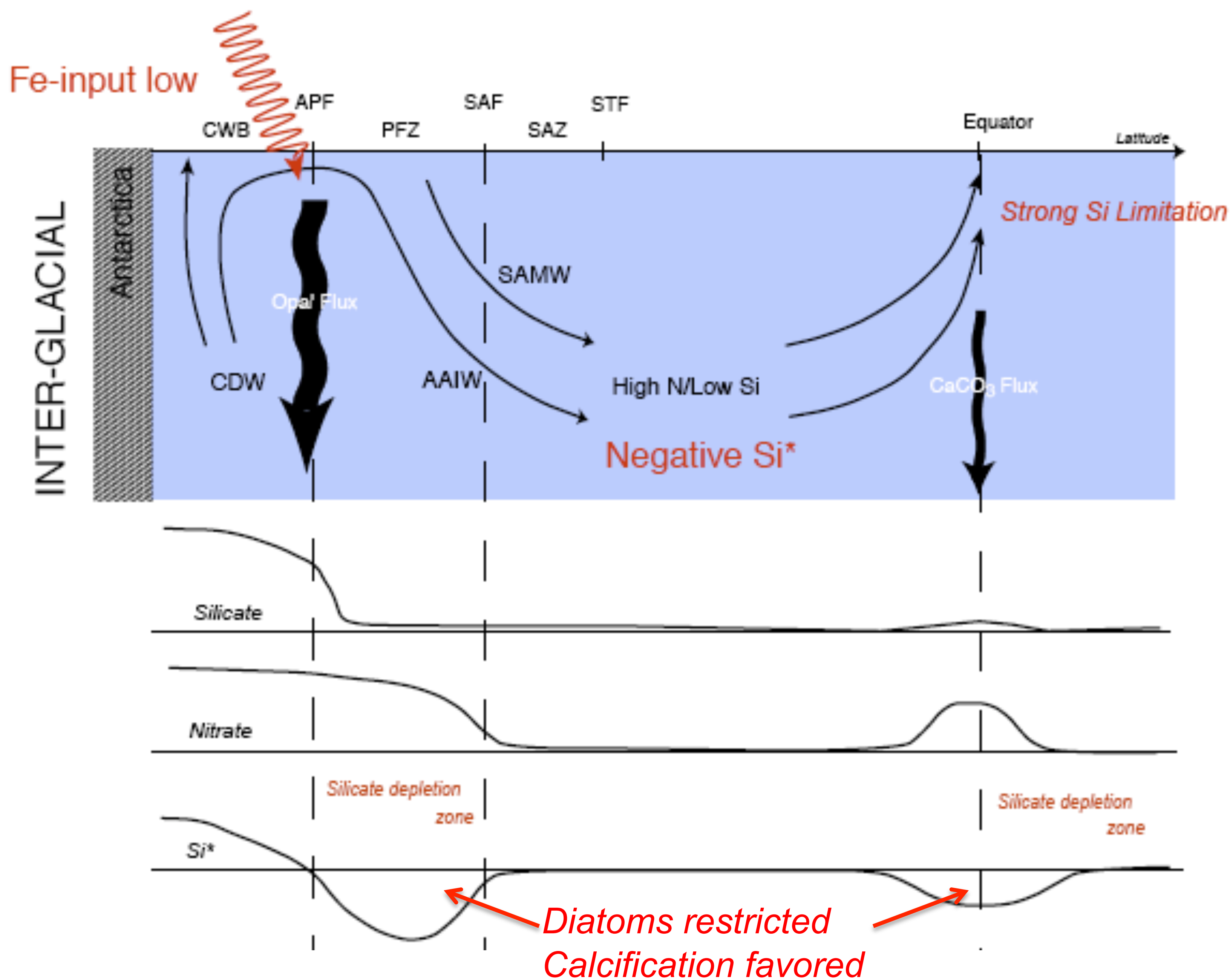
If we want to change the rain ratio of total export, we need a mechanism for altering the relative abundance of diatoms vs coccolithophorids.



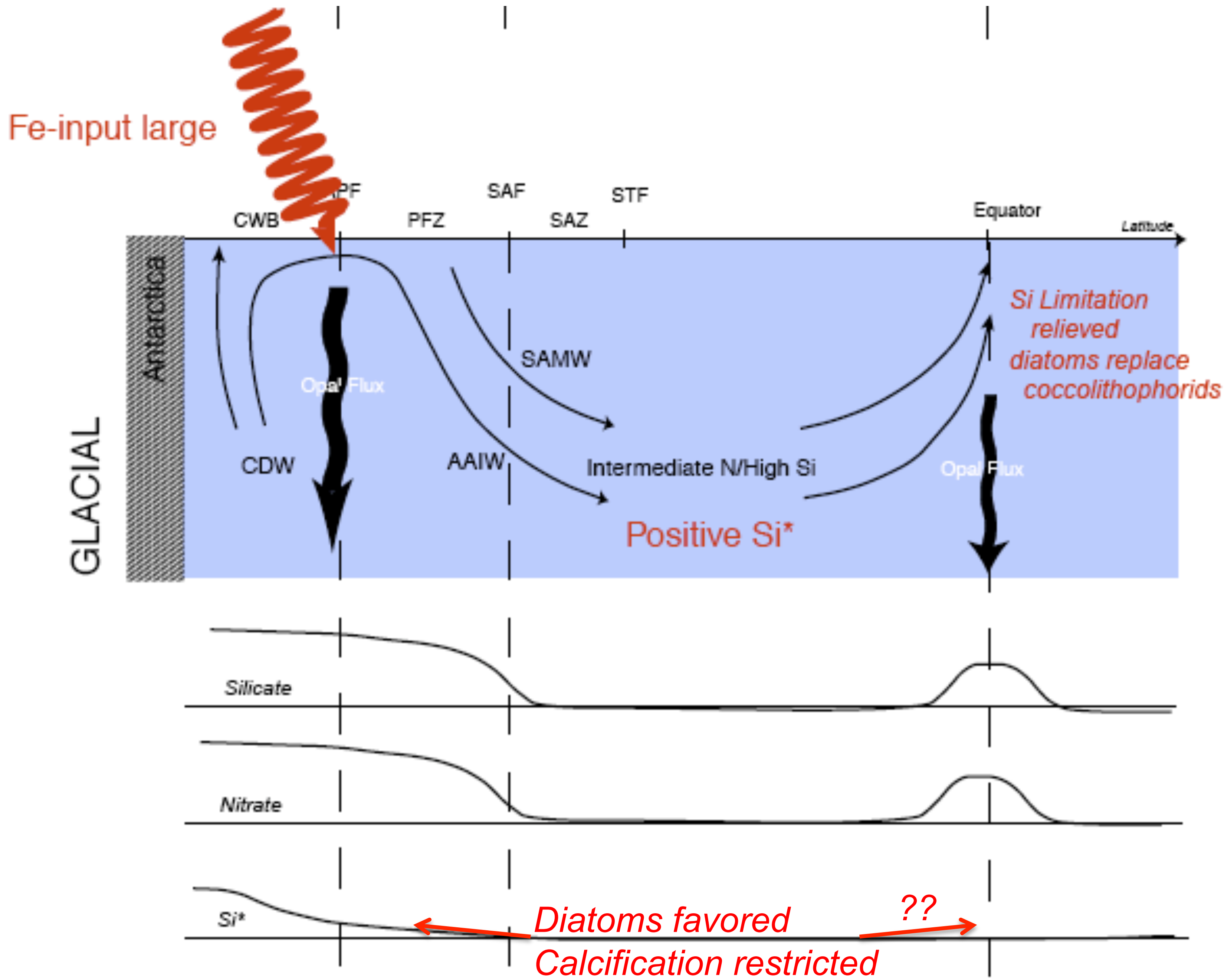
Slide: K. Matsumoto

Iron and Diatoms





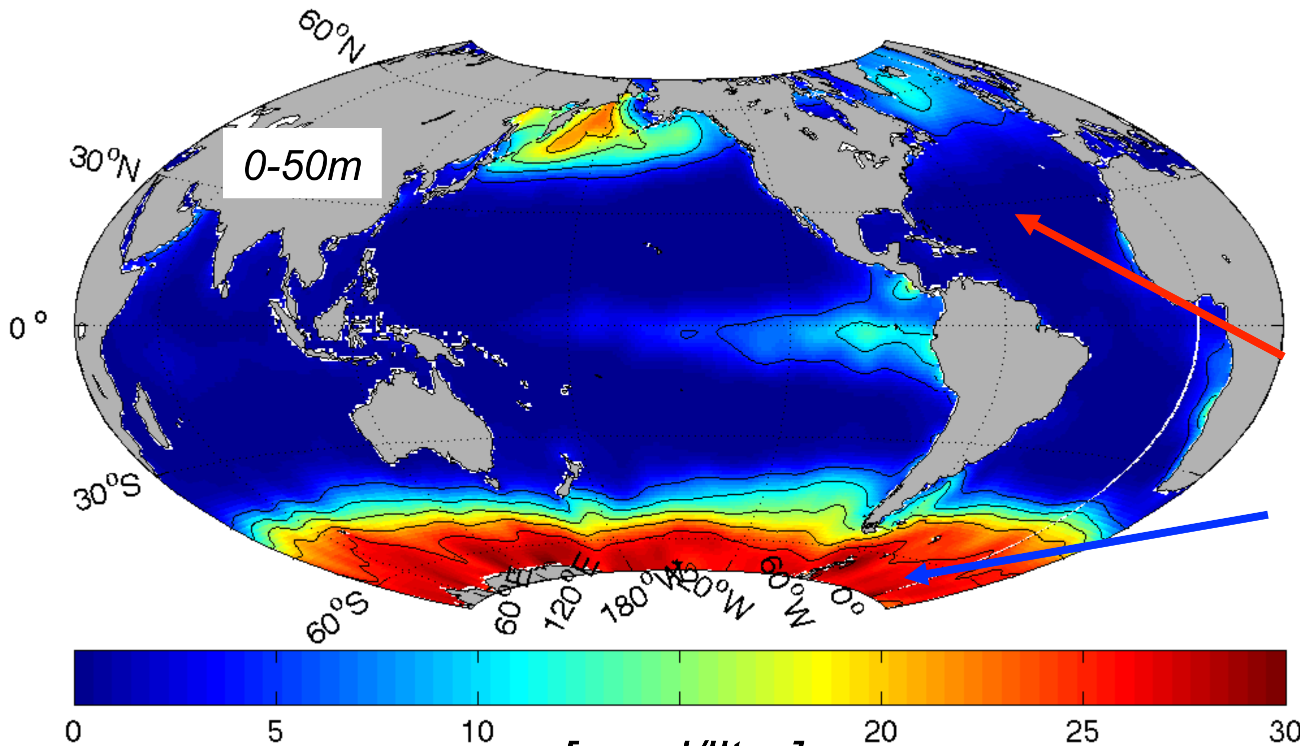
Fe-input low
INTER-GLACIAL
Antarctica
CWB
APF
PFZ
SAF
SAZ
STF
Equator
Latitude
Strong Si Limitation
SAMW
Opal Flux
CDW
AAIW
High N/Low Si
CaCO3 Flux
Negative Si*
Silicate
Nitrate
Silicate depletion zone
Silicate depletion zone
Si*
Diatoms restricted
Calcification favored



Fe-input large
GLACIAL
Antarctica
CWB
PF
PFZ
SAF
SAZ
STF
Equator
Latitude
SAMW
Opal Flux
CDW
AAIW
Intermediate N/High Si
Positive Si*
Si Limitation relieved
diatoms replace coccolithophorids
Opal Flux
Silicate
Nitrate
Si*
Diatoms favored
Calcification restricted
??

Did the nutrient inventory change?

Annual mean surface [NO_3^-]



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1) *Nutrient reservoir (low latitudes)*
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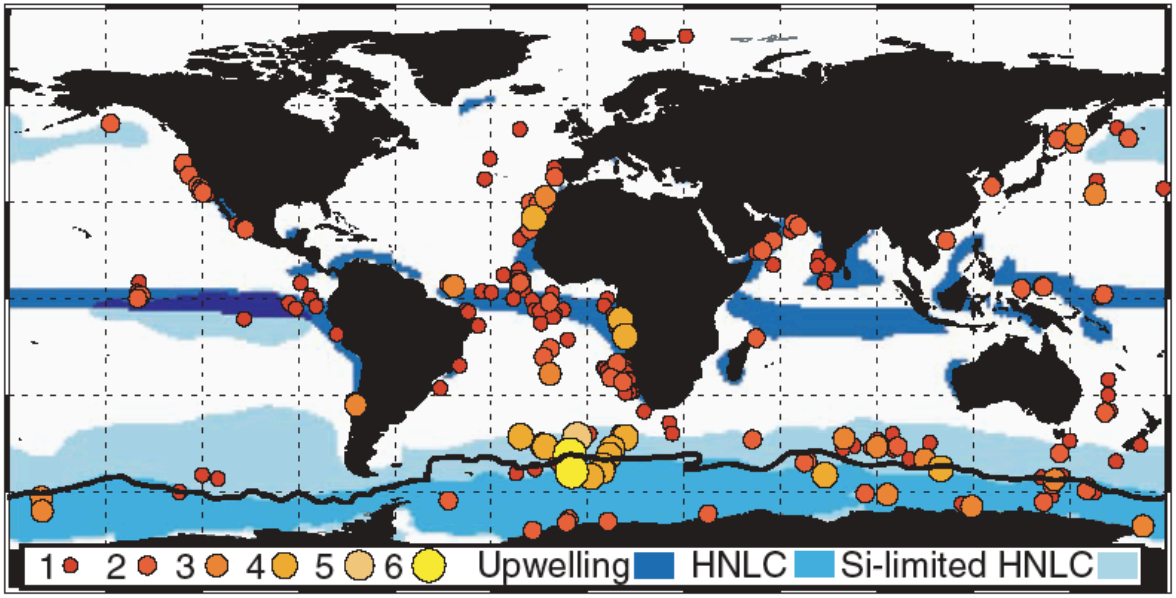
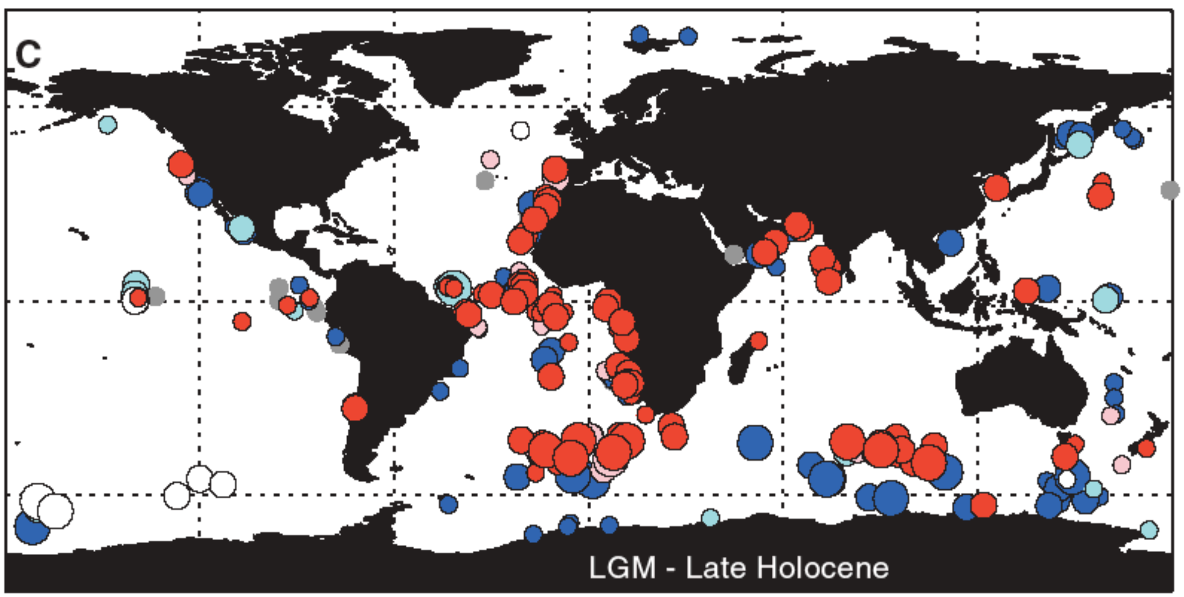
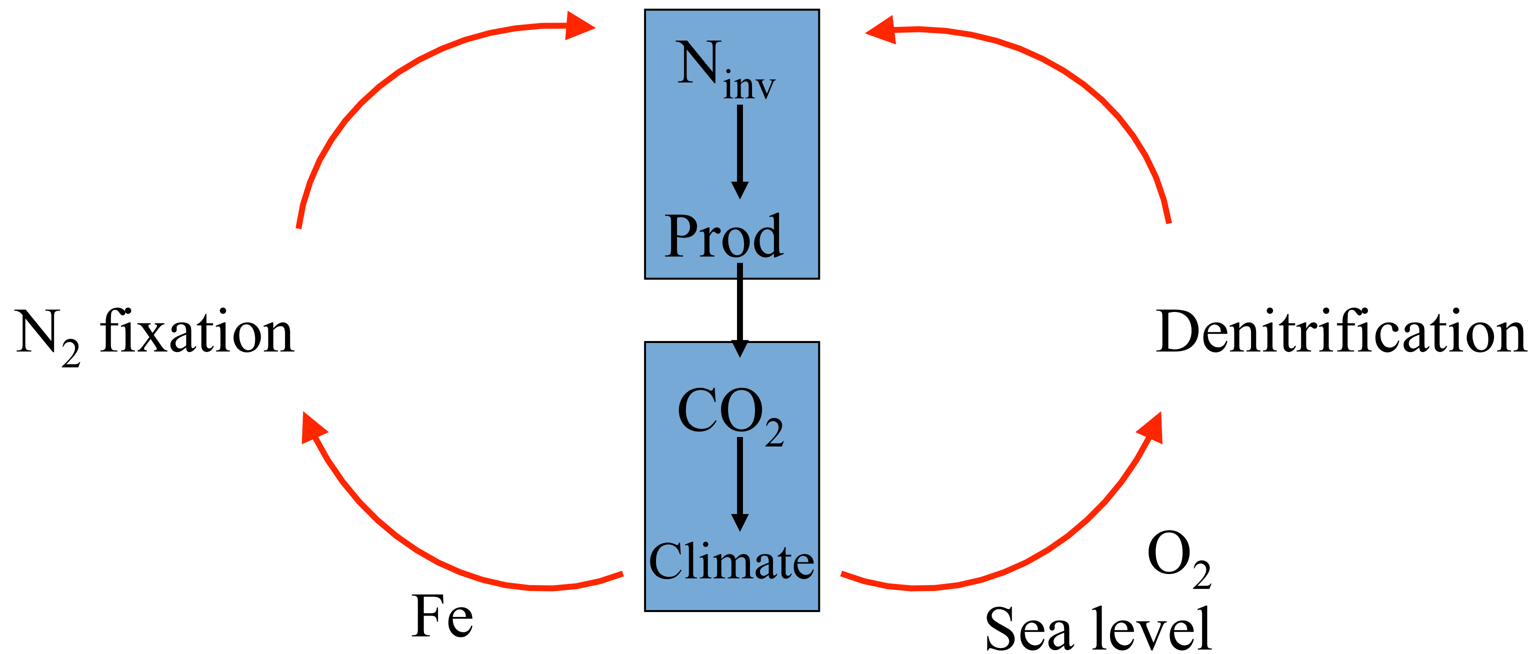
Glacial Productivity





Oceanic N as Climate Amplifier



Falkowski [1997]
Broecker + Henderson [1998]

Altabet et al. [1995]
Ganeshram et al. [1995]

N cycle could amplify climate perturbations via effect on productivity and atmospheric CO_2.

Glacial/Interglacial N hypotheses

- Glacial water column denitrification was lower

  Ganeshram et al [1995], Altabet et al. [1995]

- Glacial sediment denitrification was lower

  Christensen et al. [1987]

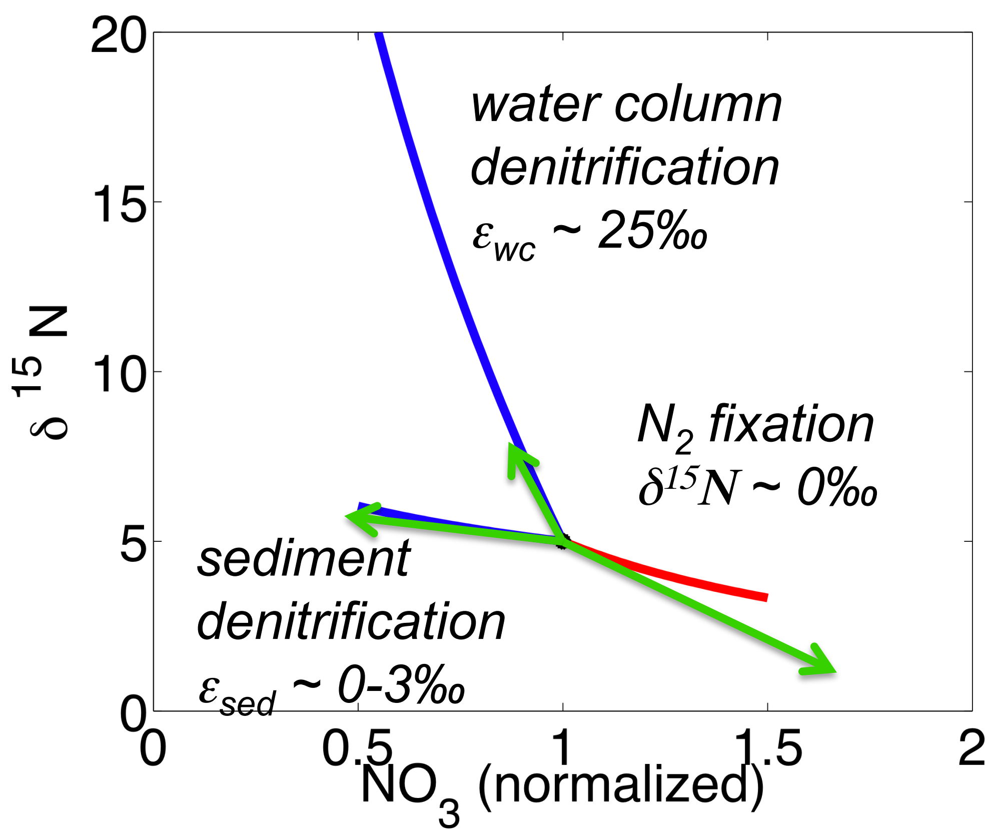
- Glacial N_2 fixation was higher

  Falkowski [1997], Broecker and Henderson [1998]

→ Pacing of change on G/I time scale

→ Huge G/I deviations in nitrogen inventory

Nitrogen Budget via Isotopes



$$V_{oc}\frac{dN}{dt} = F - W - B$$

$$V_{oc}\frac{d^{15}N}{dt} = \alpha_F F R_{air} - \alpha_W W R - \alpha_B B R$$

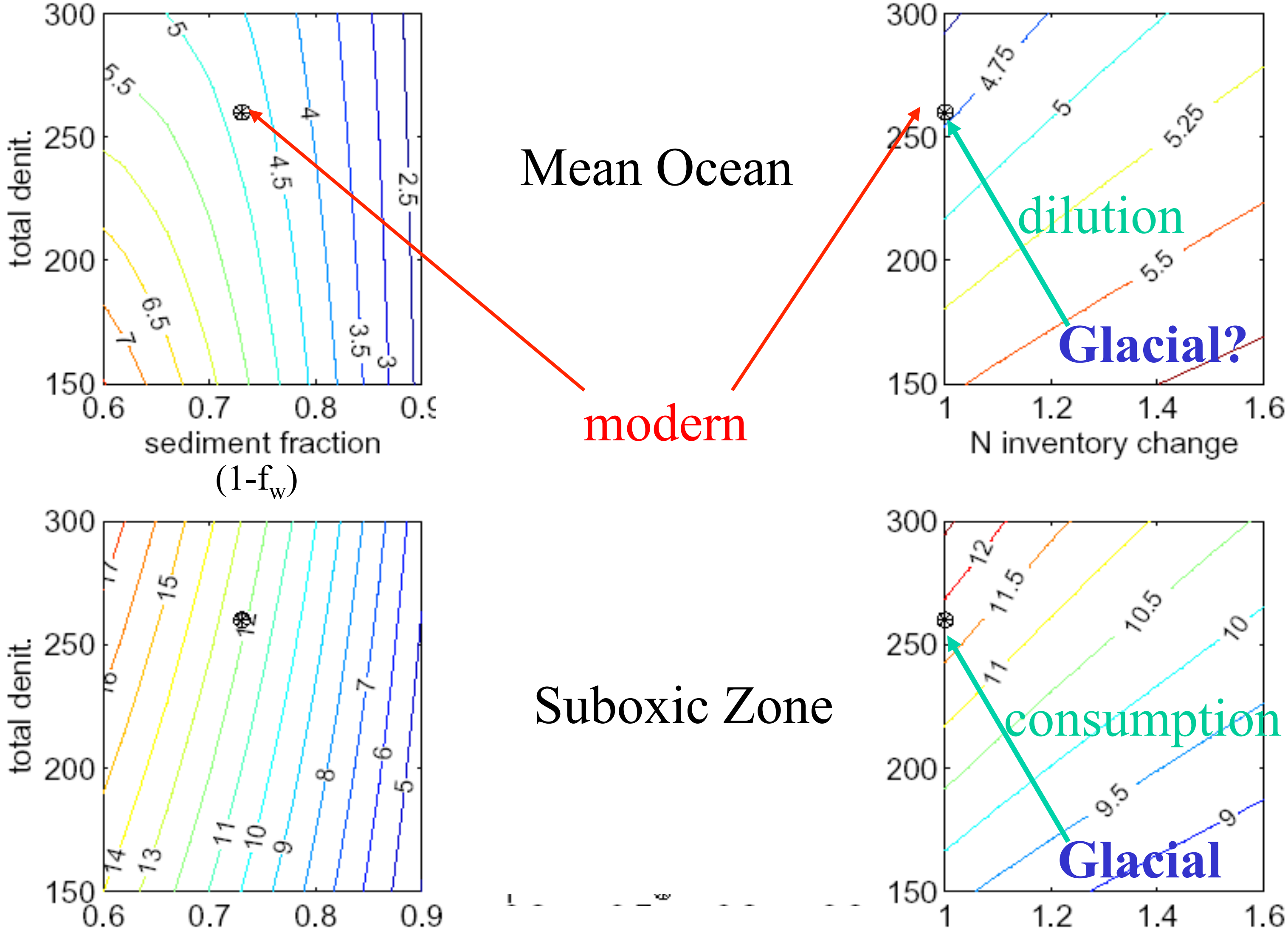
$$\boxed{\delta \sim \frac{R}{R_{air}} = \frac{1}{f_w \alpha_w + (1 - f_w)\alpha_B}}$$

Uncertainty in Sed. Denit.:

$$\frac{\partial B}{\partial \varepsilon_{wc}} = \frac{W}{\delta^{15}N} \approx \frac{15\ \text{TgN/yr}}{1\ \text{permil}}$$

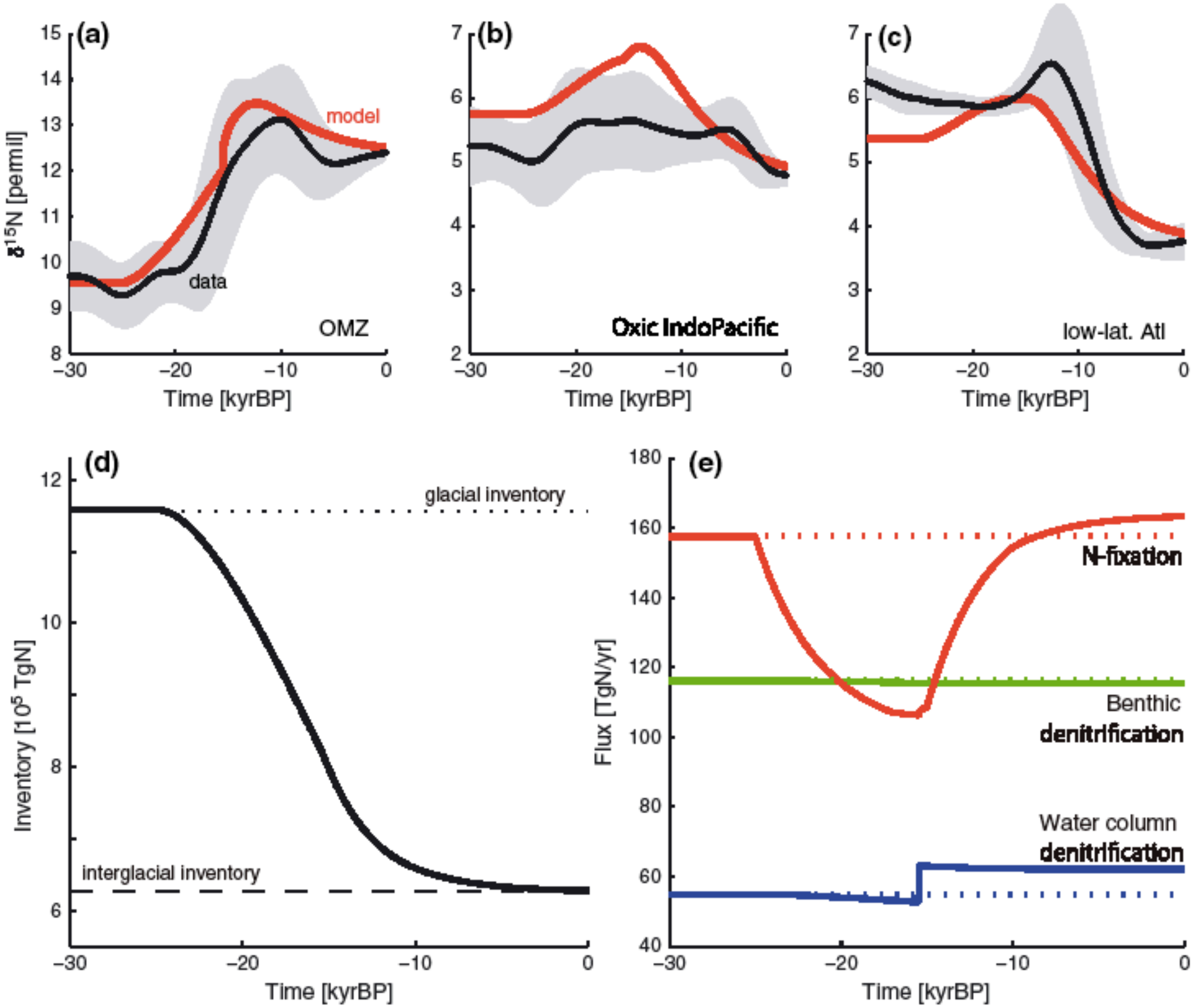
Mean ocean $\delta^{15}N$ of NO_3 reflects the balance of denitrification in sediments.
Implies large N losses, more than known fixation!
But the constraint is very sensitive to uncertainties in WCD and ε_{wc}.

Isotopic Constraints



Deutsch et al. [2004]

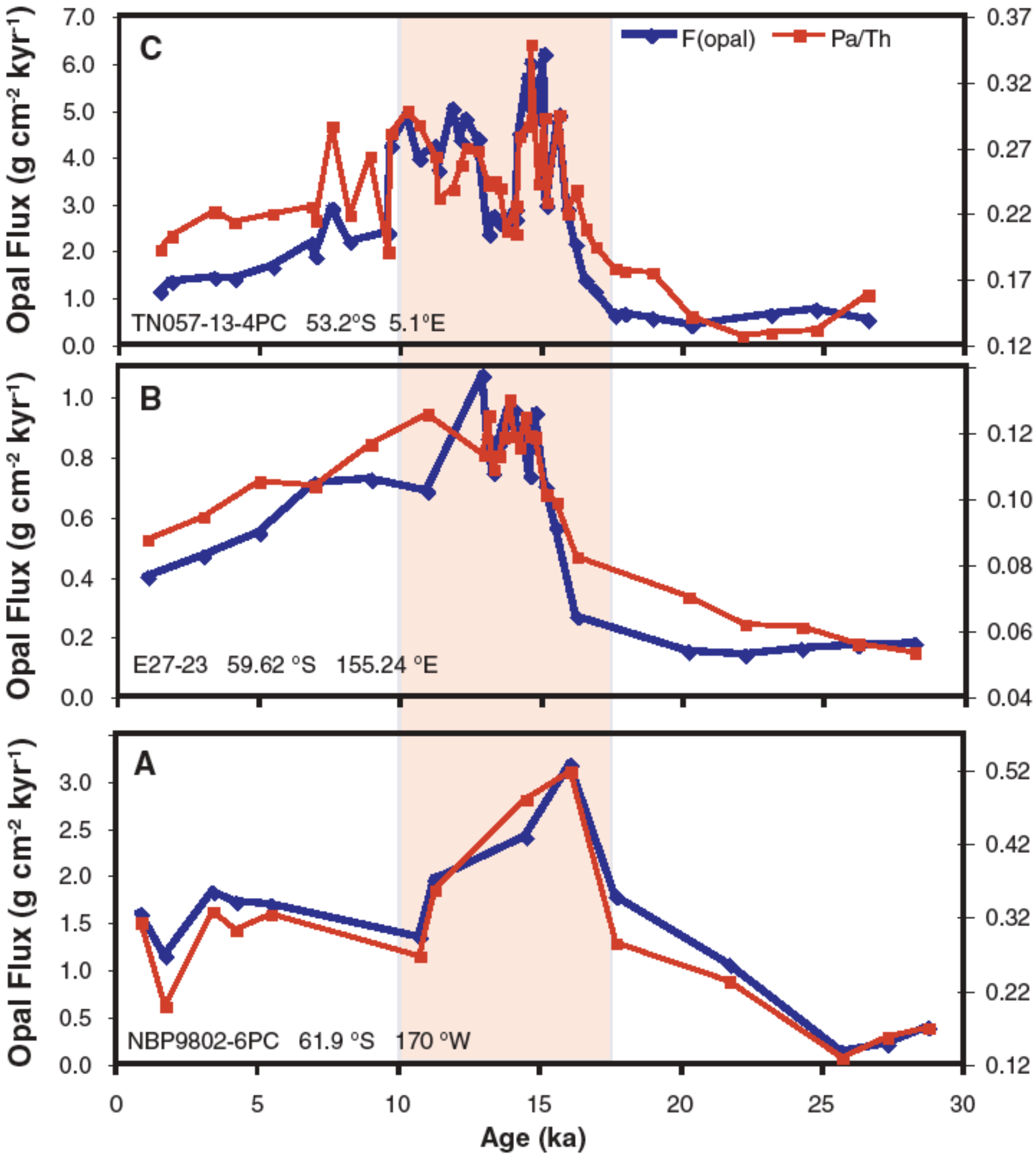
A large glacial N reservoir?



Eugster et al. [2013]

Summary

- Explaining the low atmospheric CO2 during the ice ages is critical, but hard. Lots of mechanisms proposed, but no silver bullet.
- Role of the Southern Ocean is central, since it currently has low nutrient utilization, but drivers of greater efficiency unclear.
- Several potential mechanisms can contribute 20-30ppm, but timing and sequence and also relevant.



C
F(opal)
Pa/Th
TN057-13-4PC 53.2°S 5.1°E
B
E27-23 59.62 °S 155.24 °E
A
NBP9802-6PC 61.9 °S 170 °W
Opal Flux (g cm-2 kyr-1)
Age (ka)