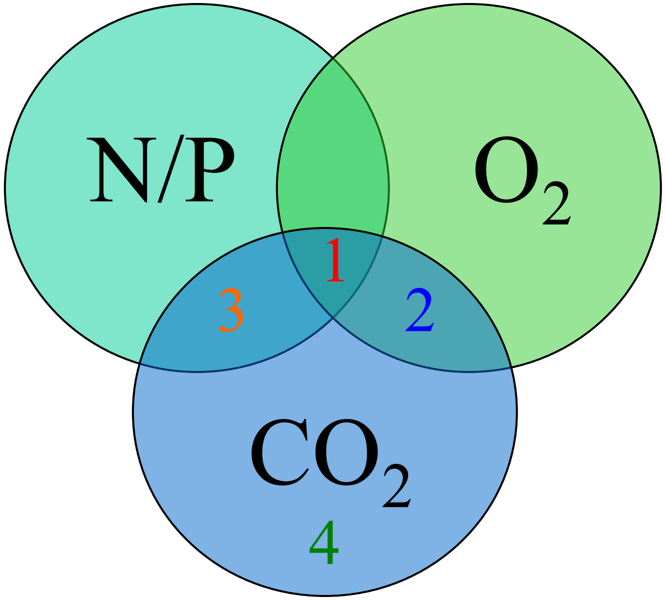
Biogeochemical Cycles



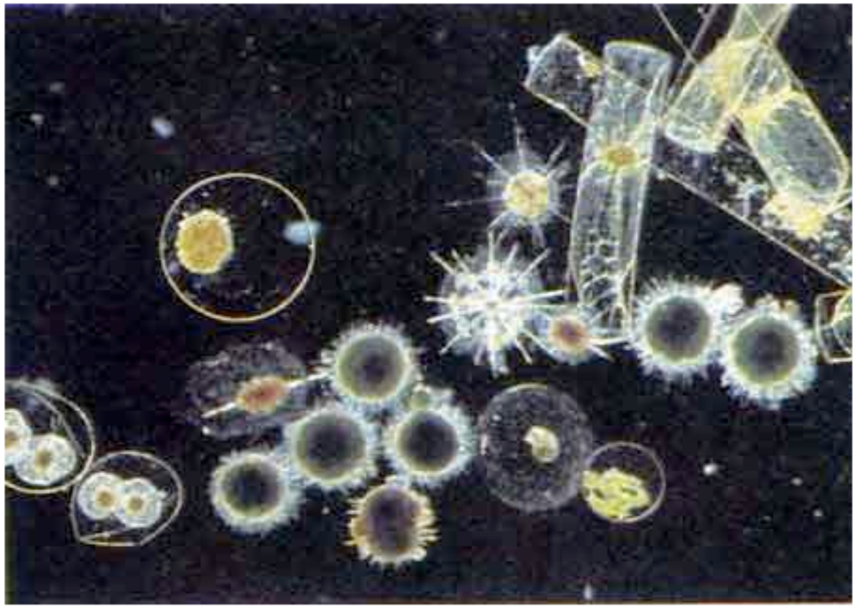
1) Biological cycling
2) Gas exchange
3) Global sources/sinks
4) Chemical reactions

…and circulation,
of course.

WF: Chap. 5: Biological Fundamentals
“ ” 6: Carbonate Chemistry Fundamentals

Biological coupling of element cycles:

the equation of life in the oceans



The elemental composition of average marine plankton

$$106CO_2 + 16HNO_3 + H_3PO_4 + 78H_2O$$

photosynthesis/ growth $\Big\downarrow \; \Big\uparrow$ remineralization/ respiration/ oxidation

$$C_{106}H_{175}O_{42}N_{16}P + 150O_2$$

Simpler version (with glucose): $6CO_2 + 6H_2O \longleftrightarrow C_6H_{12}O_6 + 6O_2$

The transformations of primary elements of life are closely connected by the biomass requirements of plankton. The proportions, known as “Redfield ratios”, are relatively constant when averaged over large plankton communities.

Composition of Phytoplankton:

Carbohydrates @ 26% : energy storage and building blocks of most cellular components (e.g., glucose).

Lipids @ 16%: energy storage and building blocks for membranes.

Proteins @ 54%: structural components and enzymes that catalyze biochemical reactions.

Nucleic acids @ 4%: agents of reproduction and blueprints for development.

The Biological Pump:

The recycling exchanges between organic matter, mostly created in the euphotic zone from light and inorganic nutrients, and inorganic matter, created by remineralization/ respiration/decay, mostly by the action of bacteria on dead organic matter, both in the interior and in the euphotic zone.

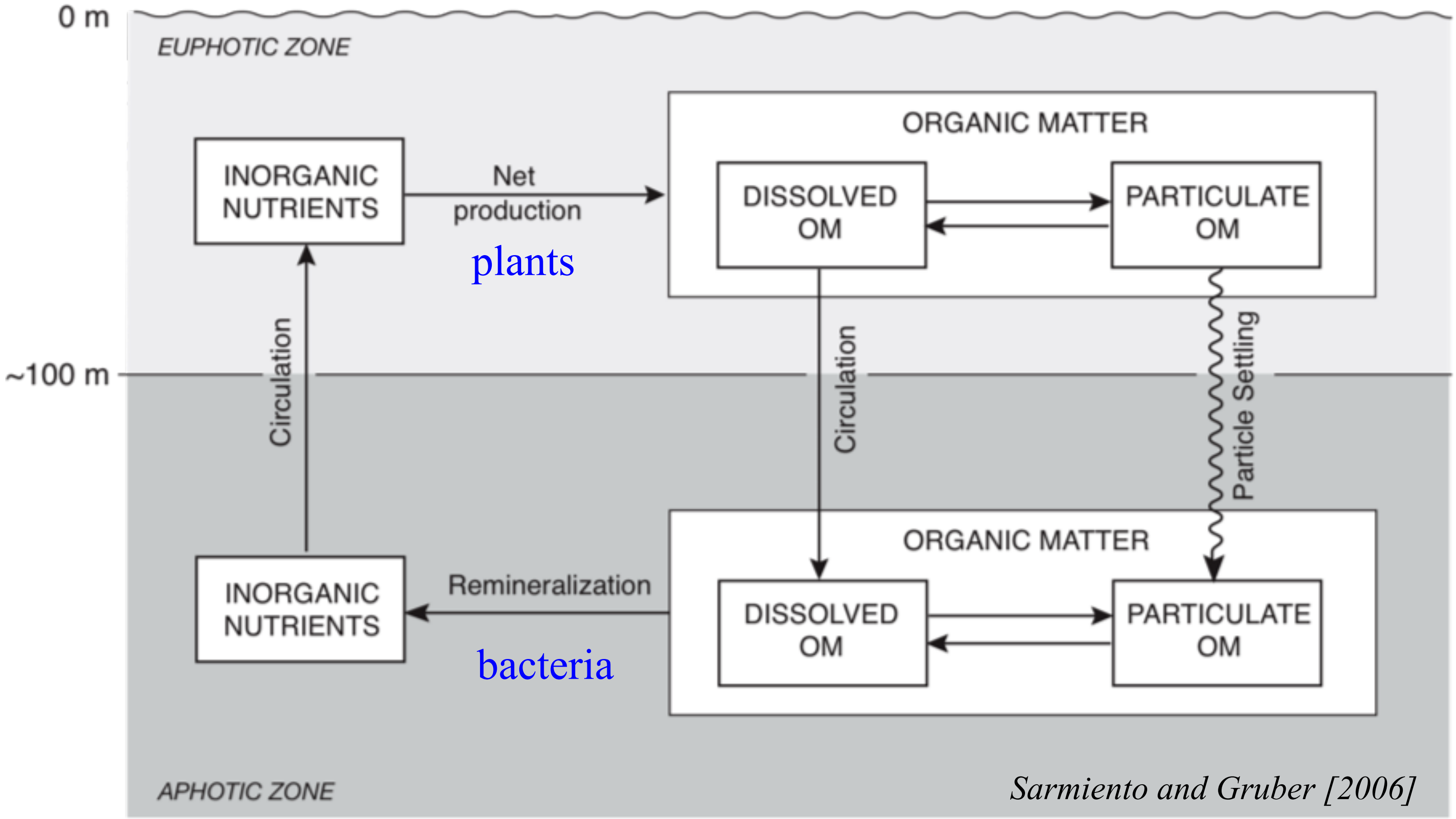
The Food Web:

Autotrophs: organisms that can create organic matter directly from inorganic matter.

Heterotrophs: organisms that gain energy and nutrition only from organic matter.

… and then there are Mixotrophs.

Nutrient cycles

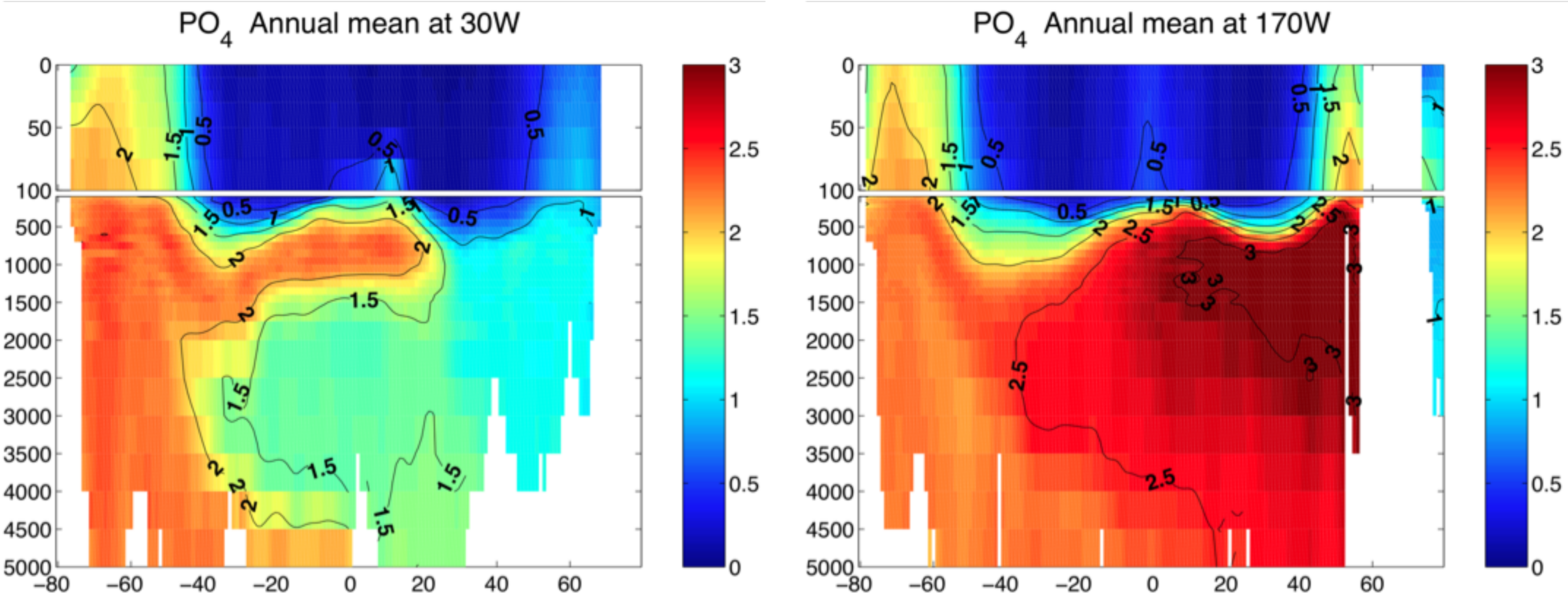


Sarmiento and Gruber [2006]

Schematic depiction of biogeochemical cycling of nutrients between simple inorganic molecules and complex (and innumerable) organic compounds. Organic matter (OM) is formed primarily through photosynthesis in the surface ocean (<100m). [P]articles of OM are subject to sinking, while [D]issolved OM is transported only by the flow. POM vs. DOM is defined operationally by size. Much of the remineralization occurs within the euphotic zone as local recycling.

Dissolved Nutrients

1) Phosphate section



Depth-Latitude section of phosphate (PO_4 [mmol/m^3], the sole form of dissolved inorganic phosphorus) along 30W in the Atlantic and 170W in the Pacific from World Ocean Atlas [2005]. Upper ocean is depleted in PO_4 due to its uptake by plankton for photosynthesis. Deep ocean has high PO_4 due to remineralization of organic P, increasing from NADW to NPDW. High polar values are due to vertical exchange.

Concept: Oceanic biogeochemists use a variety of units to express fractional concentration ... a tower of Babel.

It helps to stick with SI units:A basic unit is a molar mass, often abbreviated as [mole] or [mol].

1 mole = atomic mass X 10−3 kg/mole [kg].

Mass fraction is relative to seawater [mol/kg, which is non-dimensional]. This can alternatively be expressed as a mass density after multiplying by seawater density $\rho_0 \approx 1025$ kg/m^3 [kg/m^3].

E.g., O_2 = 300 mmol/m^3 = 300 X 10^{-3} X 2·16 X 10^{-3} = 0.96 $\times 10^{-2}$ kg O/m^3.

DIC = 2075 μmol/kg = 2075 X 10^{-6} X 12 X 10^{-3} X 1025 = 2.55 $\times 10^{-2}$ kg C/m^3.

Concept: A common chemical notation for isotope abundance is the relative anomaly, often expressed in o/oo:

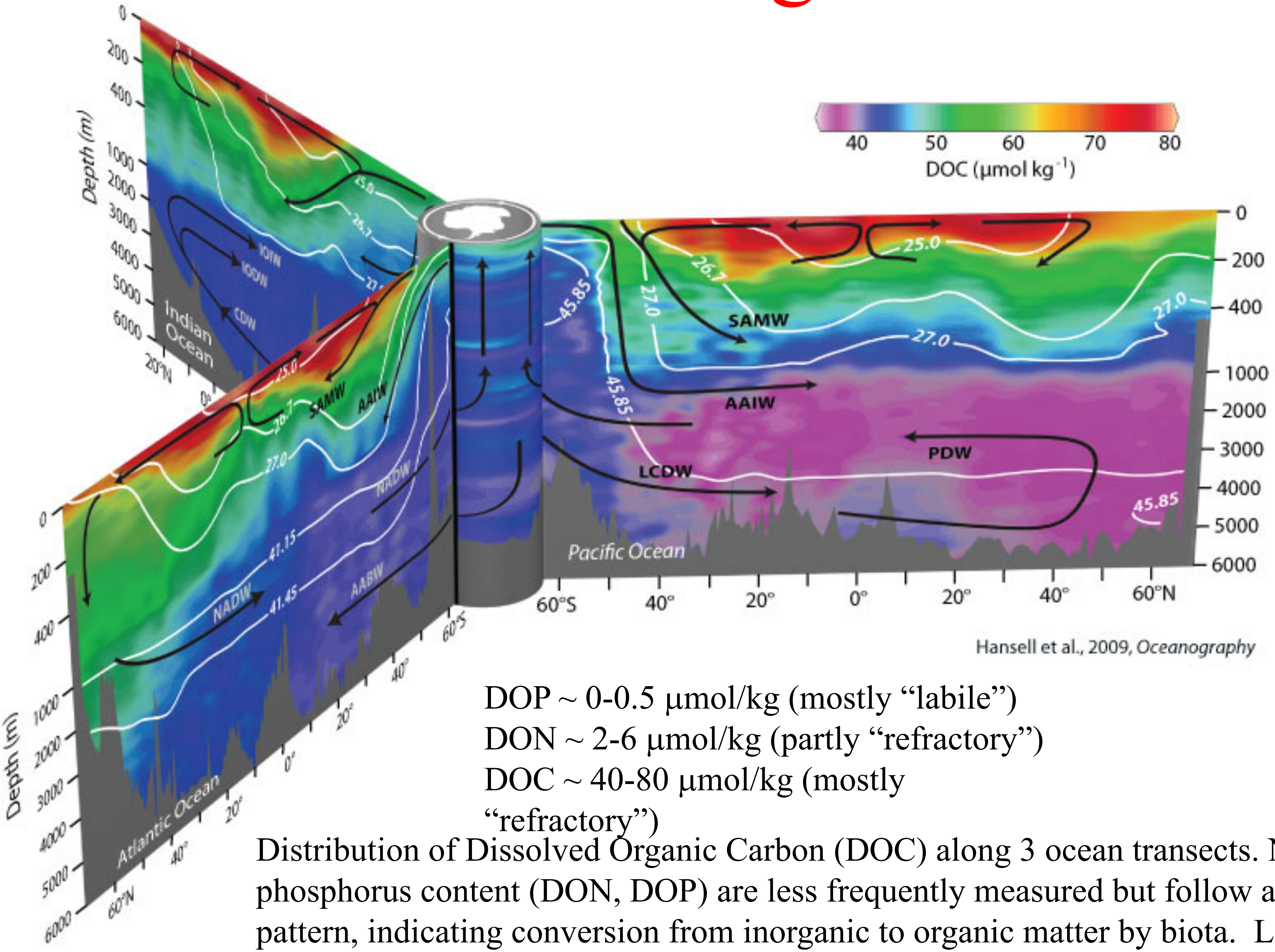
For a quantity c, δc or $\Delta c = \dfrac{c_{in\ situ} - c_{standard}}{c_{standard}}$,

where the standard is either the preindustrial atmosphere as recorded in old wood samples (for $\Delta\ ^{14}C$) or Standard Mean Ocean Water (SMOW) (for O_2, H_2) or air (for N_2), *etc.*

E.g., for $\Delta\ ^{14}C$, the value of - 150 o/oo means a relative anomaly of - 0.15.

See S. Emerson and J. Hedges, 2008: *Chemical Oceanography and the Marine Carbon Cycle.* Cambridge Press.

Dissolved Organic Matter

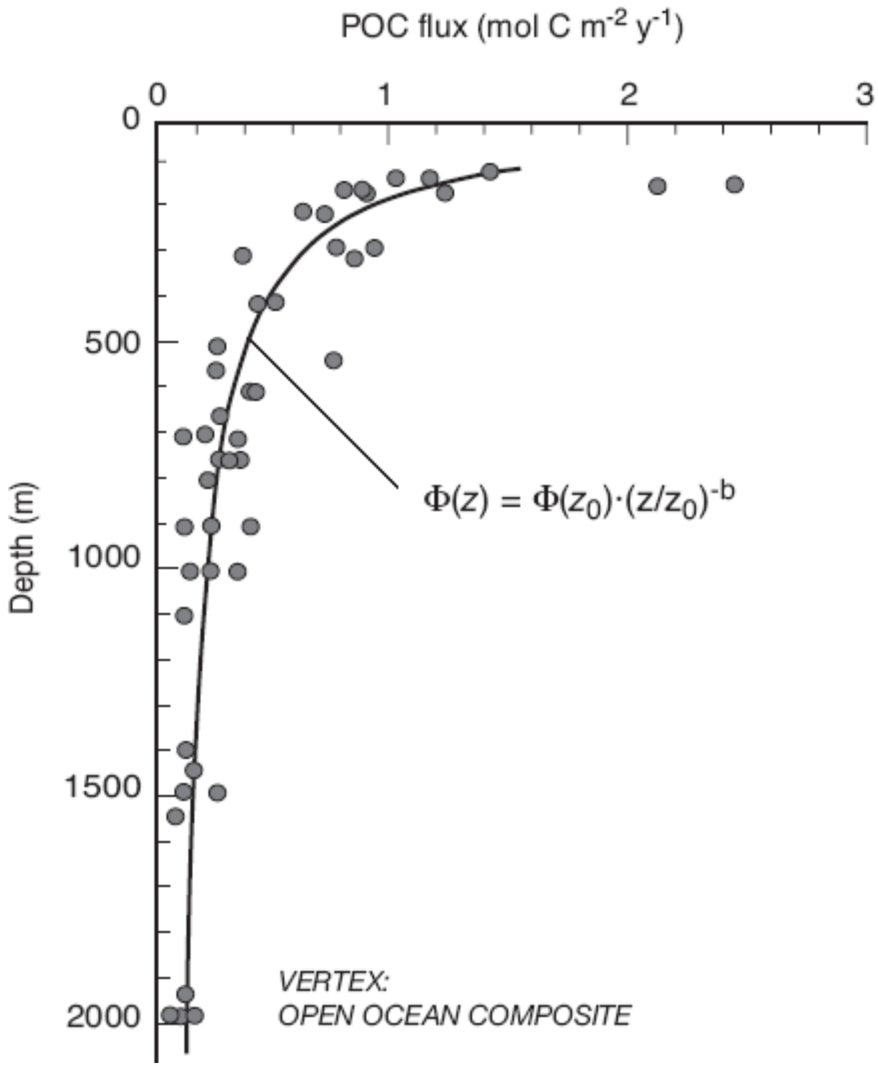


Hansell et al., 2009, *Oceanography*

DOP ~ 0-0.5 μmol/kg (mostly "labile")
DON ~ 2-6 μmol/kg (partly "refractory")
DOC ~ 40-80 μmol/kg (mostly "refractory")

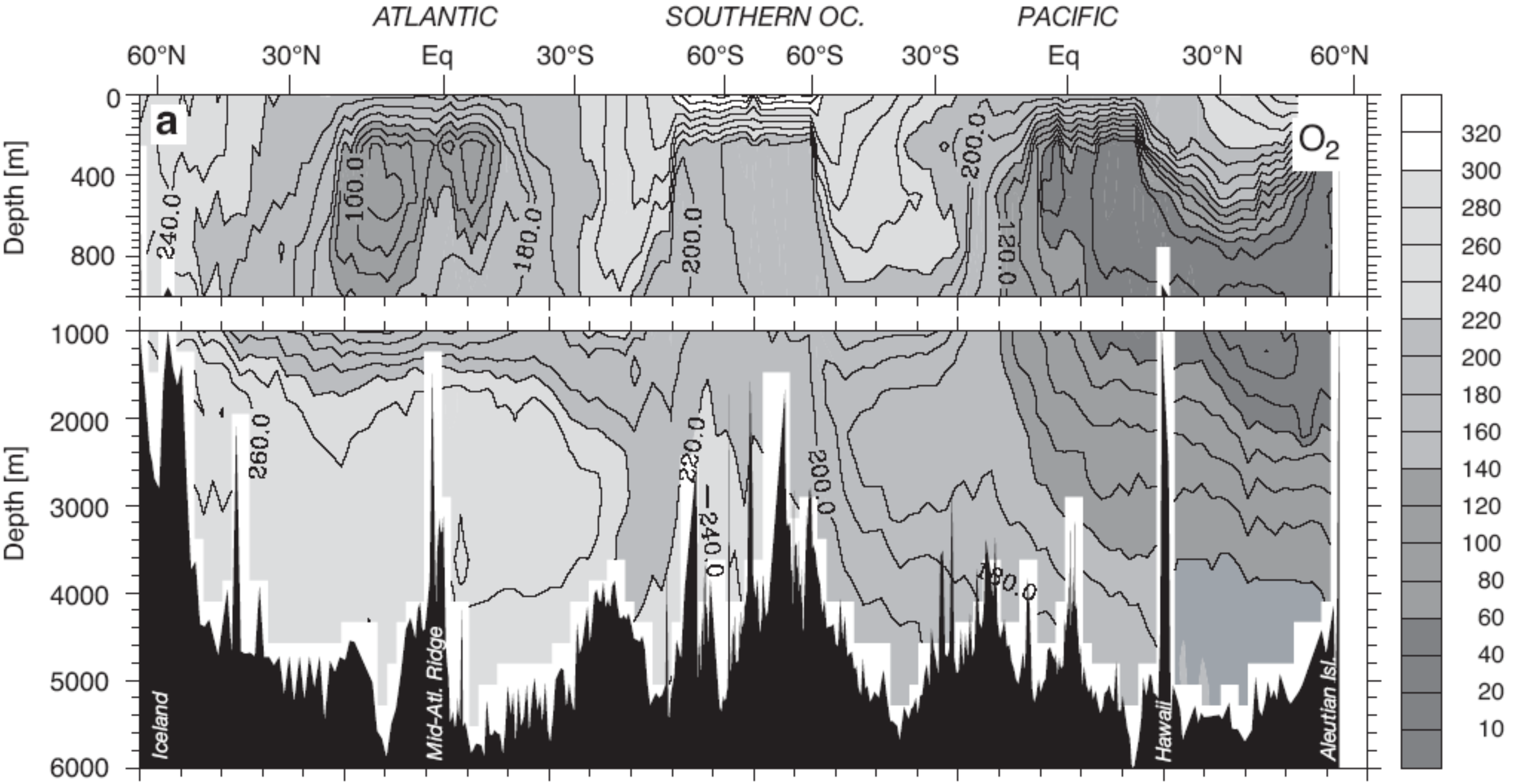
Distribution of Dissolved Organic Carbon (DOC) along 3 ocean transects. Nitrogen and phosphorus content (DON, DOP) are less frequently measured but follow a similar pattern, indicating conversion from inorganic to organic matter by biota. Lowest values indicate the component of DOM that is resistant to uptake/degradation ("refractory").

Particle flux



The flux of sinking particles measured in sediment traps, at sites in the Eastern Pacific. The decrease with depth (flux divergence) is a measure of rates of organic matter respiration/remineralization. The vertical structure may depend on temperature, particle size and composition, O_2, bacteria, etc. Rates of remineralization get slower with depth. Horizontal variations are usually not directly measured, but can be inferred (e.g., from O_2) Only a tiny fraction makes it to the bottom, the benthic sediments.

Oxygen Distribution

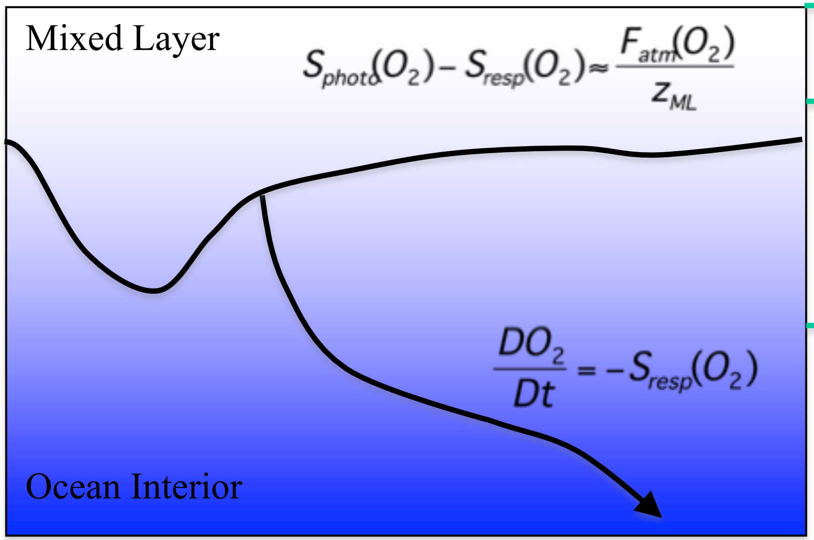


Depth-Latitude section of oxygen (O_2 [$mmol/m^3$]) from Atlantic to Pacific [SG06]. Oxygen reaches a minimum at mid-depths due to remineralization of organic matter and a long circulation pathway between ventilation exposures. This pattern is reminiscent of other global water mass measures such as S and ^{14}C, though with quantitative differences.

Oxygen Processes

$$\frac{DO_2}{Dt} = S_{photo}(O_2) - S_{resp}(O_2) + \frac{F_{atm}(O_2)}{z_{ML}}$$

Photosynthesis Respiration Gas Exchange



$$F_{atm}(O_2) = -k_w O_2^{diseq}$$

$$O_2^{ML} = O_2^{sat}(T,S) + O_2^{dise}$$

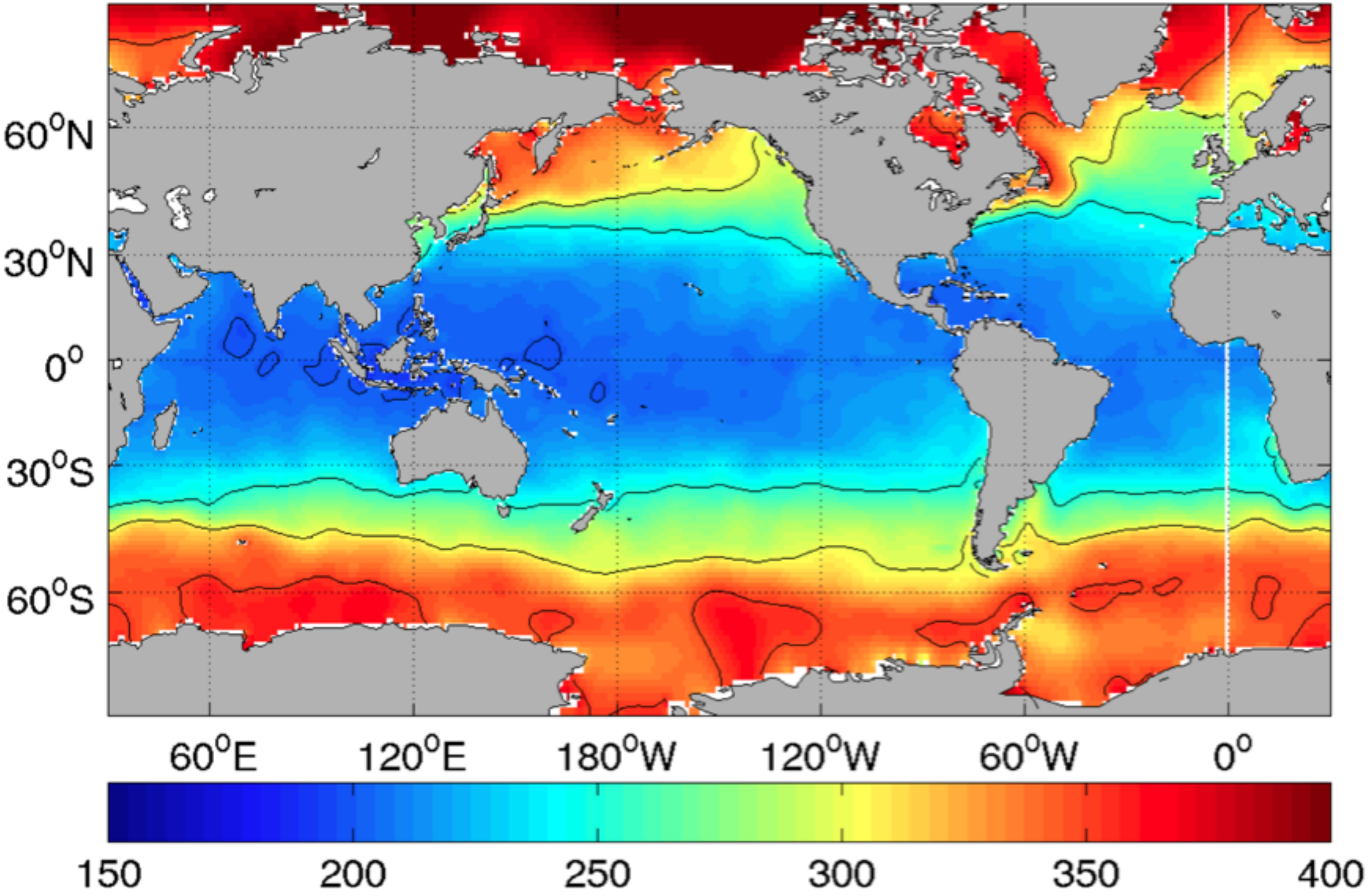
Solubility Disequilibrium

$$O_2^{Int} = O_2^{ML} - O_2^{resp}$$

Respiration

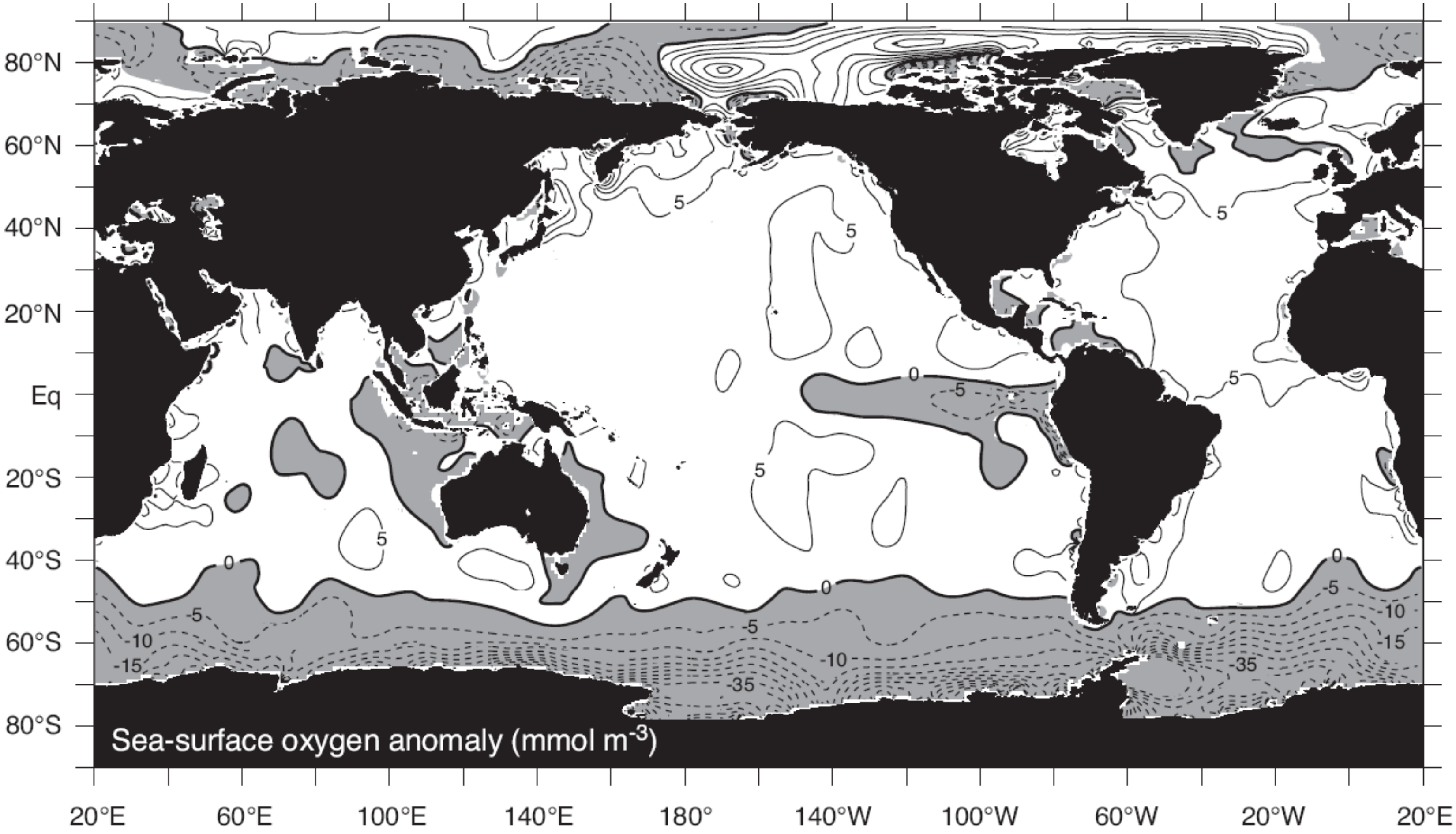
Oxygen concentration reflects different biological/physical balances:
In mixed layer (depth z_{ML}), photosynthesis balances gas exchange. In F, k_w is the transfer coefficient, called the piston velocity [m s^{-1}]. In oceanic interior, respiration is balanced by circulation and mixing transports.

Surface Oxygen



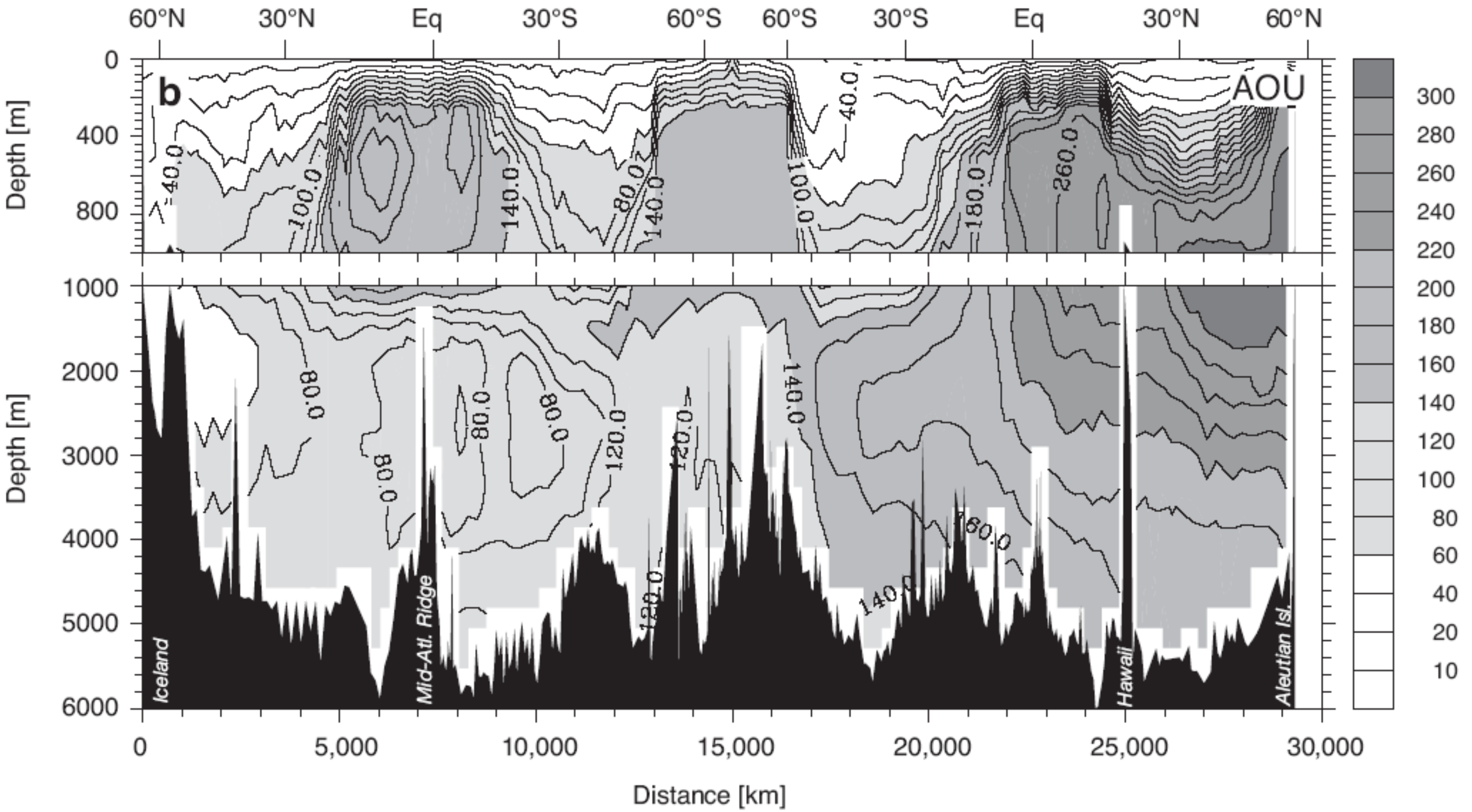
Annual mean oxygen (O_2 [mmol/m^3]) in the upper 50 m, from World Ocean Atlas [2005]. The close correspondence to SST reflects the (inverse) relationship between temperature and solubility, and the near equilibrium with the atmosphere (Henry's law): $O_2^{sat} = S\ pO_2^{atm}$, where S ~ 1500 mmol m^{-3} atm^{-1} is the solubility for oxygen; for most gases, $\partial S / \partial T < 0$.

Surface O_2 Disequilibrium



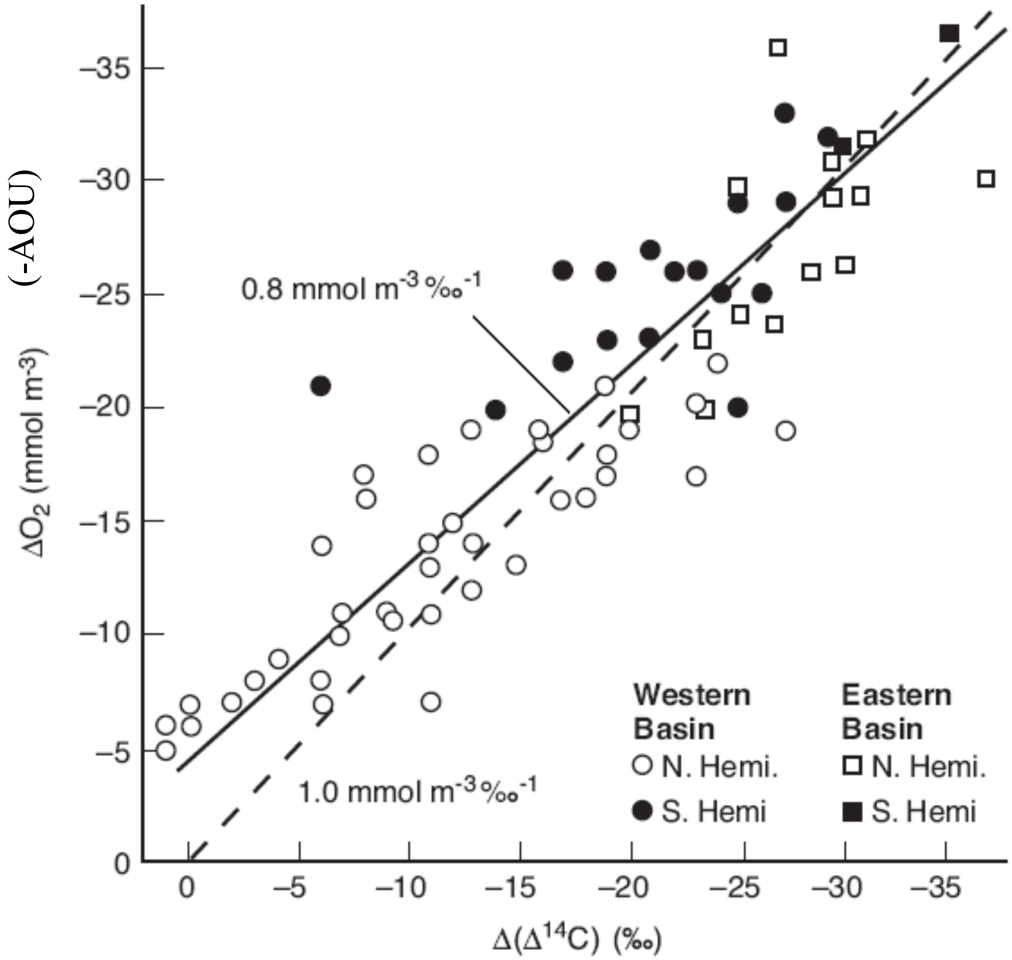
Annual mean oxygen disequilibrium, $O_2^{diseq} = - O_2^{sat} + O_2$ [mmol/m^3] in the upper 50 m, from World Ocean Atlas [2005]. Supersaturations ($O_2^{diseq}>0$) are due to heating and photosynthesis, and undersaturations ($O_2^{diseq}<0$) are due to cooling and upward transport that delay coming into equilibrium saturation with the atmosphere over a time ~ 1 month.

Apparent Oxygen Utilization



Depth-Latitude section of Apparent Oxygen Utilization (AOU = $O_2^{sat}(T,S) - O_2$, [mmol/m^3]) from Atlantic to Pacific [Sarmiento & Gruber, 2006]. AOU approximates the total amount of O_2 consumed since isolation from atmosphere, ignoring surface disequilibrium.

Deep Ocean Respiration



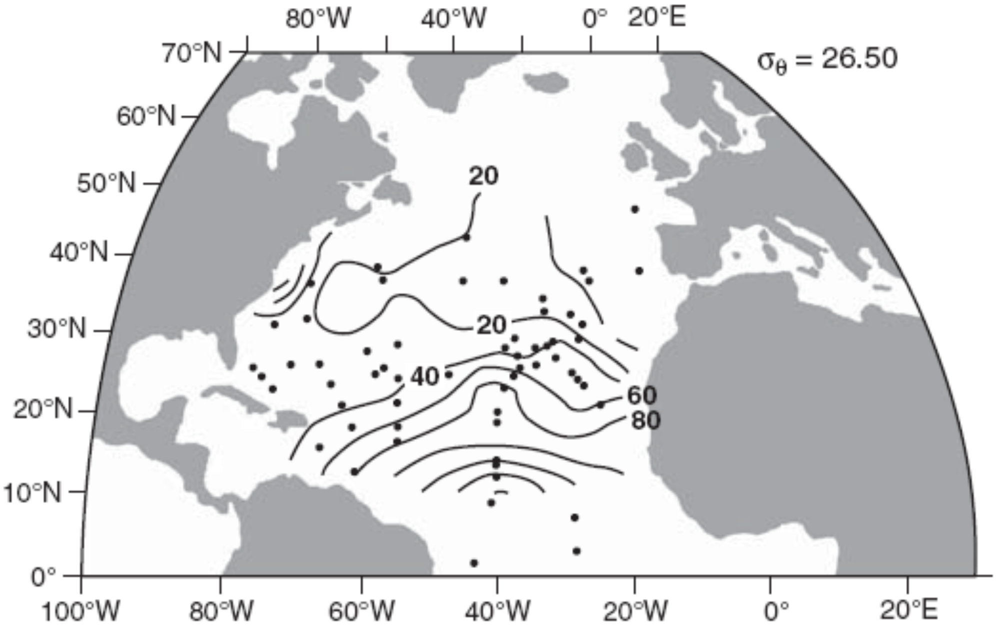
Oxygen Utilization Rate:

$$\mathrm{OUR} = \frac{\mathrm{AOU}}{\mathrm{age}}$$

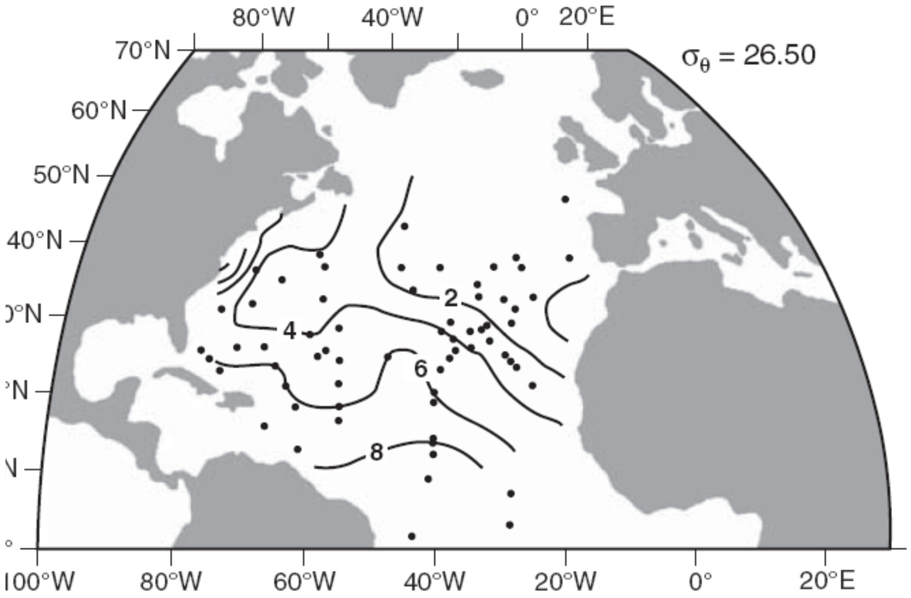
It takes ~8 years for ^{14}C to decay by 1 permil. So estimated abyssal OUR ~ 0.1 mmol/m^3/yr.

Rate of oxygen utilization due to respiration (OUR=$S_{resp}(O_2)$) can be estimated by OUR=AOU/age, where age time since isolation from the atmosphere which can be derived from transient tracers (e.g. ^{14}C, CFC, ^3H) . In the deep ocean, OUR ~ 0.1 mmol/m^3/yr.

Thermocline Respiration



AOU (mmol/m^3)



Tritium/Helium Age (yr)

Rate of oxygen utilization (OUR) due to respiration can be estimated by OUR=AOU/age, where age is derived from transient tracers (e.g. CFC, ^{3}H) . In the thermocline, OUR ~ 10 mmol/m^3/yr, ~100x larger than the deep ocean.

Conservative tracers

Starting from:

$$\frac{D(AOU)}{Dt} = S_{resp}(O_2), \quad AOU(z=0) = 0$$

$$\frac{DPO_4}{Dt} = S_{resp}(PO_4), \quad PO_4(z=0) = P_o$$

$$S_{resp}(O_2) = r_{O:P} \cdot S_{resp}(PO_4)$$

Define:

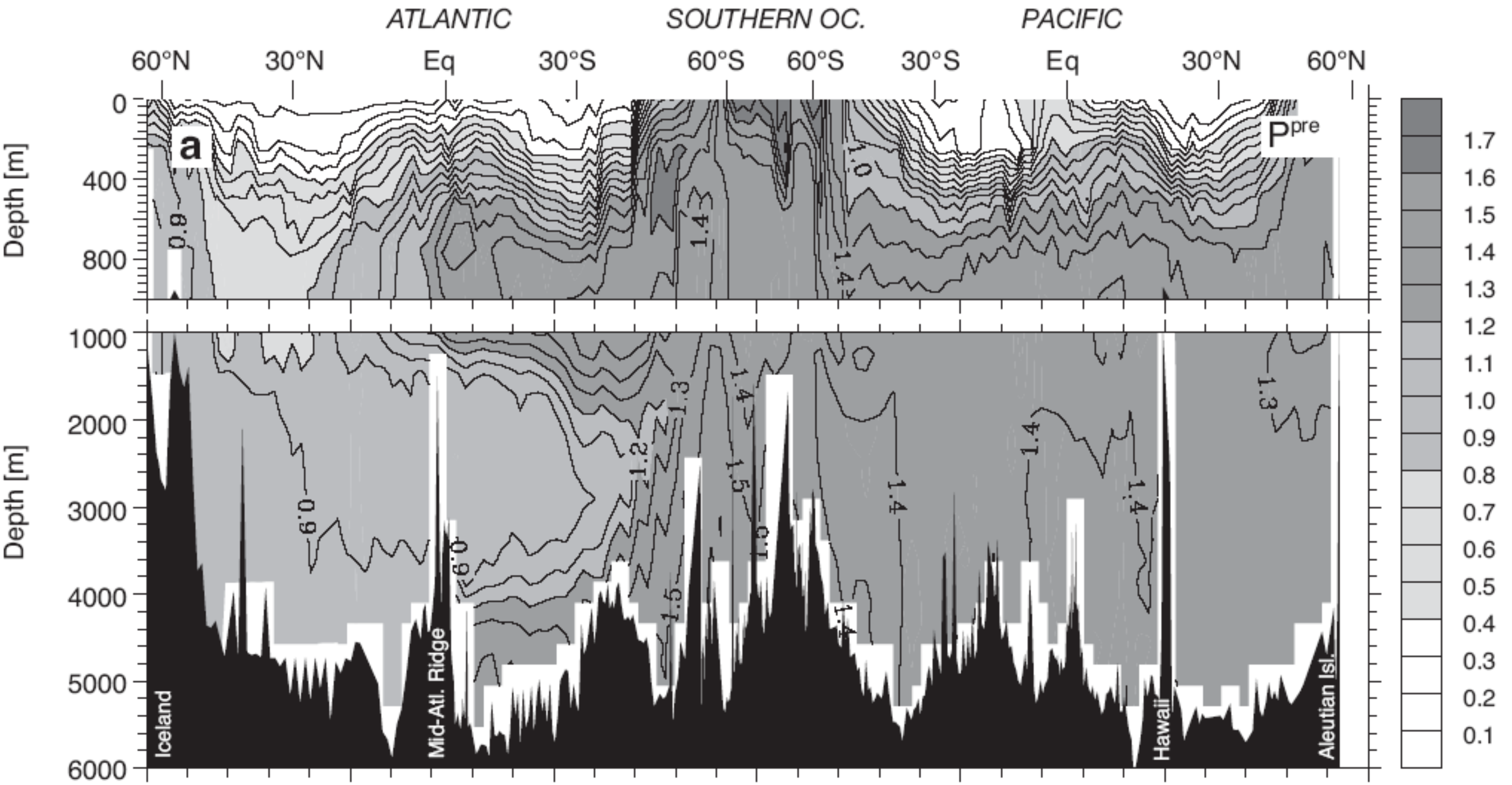
$$PO_4^{pre} = PO_4 - \frac{1}{r_{O:P}} AOU$$

Then:

$$\frac{D(PO_4^{pre})}{Dt} = 0, \quad PO_4^{pre}(z=0) = P_o$$

Oxygen and Phosphate can be combined to estimate the component of PO_4 that is transported from the surface to the interior ocean, "pre-formed" PO_4. It is a parcel-conservative water mass tracer, whose value is set at the surface and unchanged by subsurface respiration but for mixing. The Redfield value is $r_{O:P} = 150$.

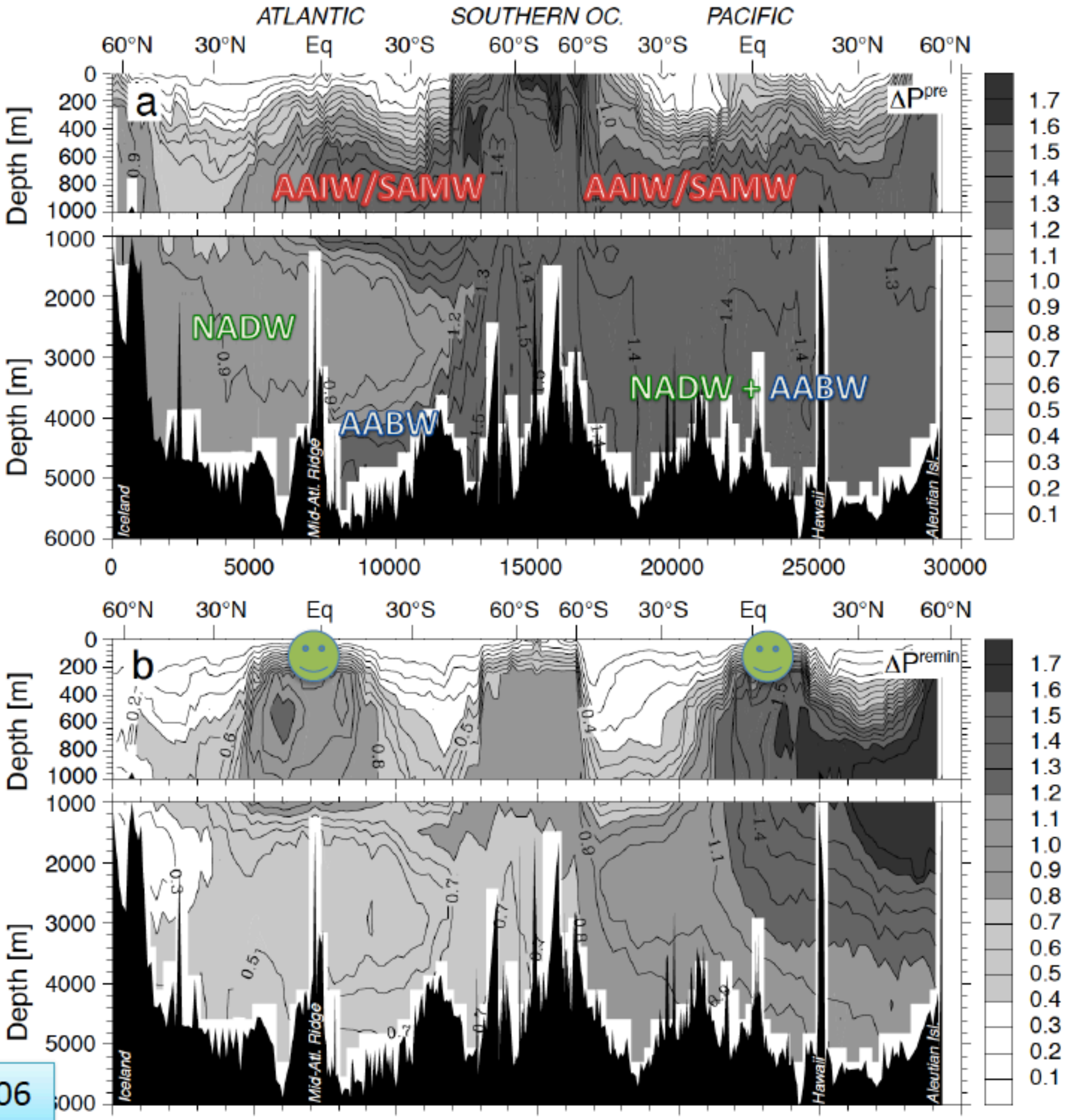
“Pre-formed” Phosphate



Depth-Latitude section of pre-formed PO_4 (PO_4^{pre}, mmol/m^3) from Atlantic to Pacific. Most of the deep ocean PO_4 arrives via transport rather than remineralization. Deep gradient understood as a tracer of Southern versus Northern water mass origins (AABW vs. NADW) that are largely preserved following the circulation. This is a repeated slide.

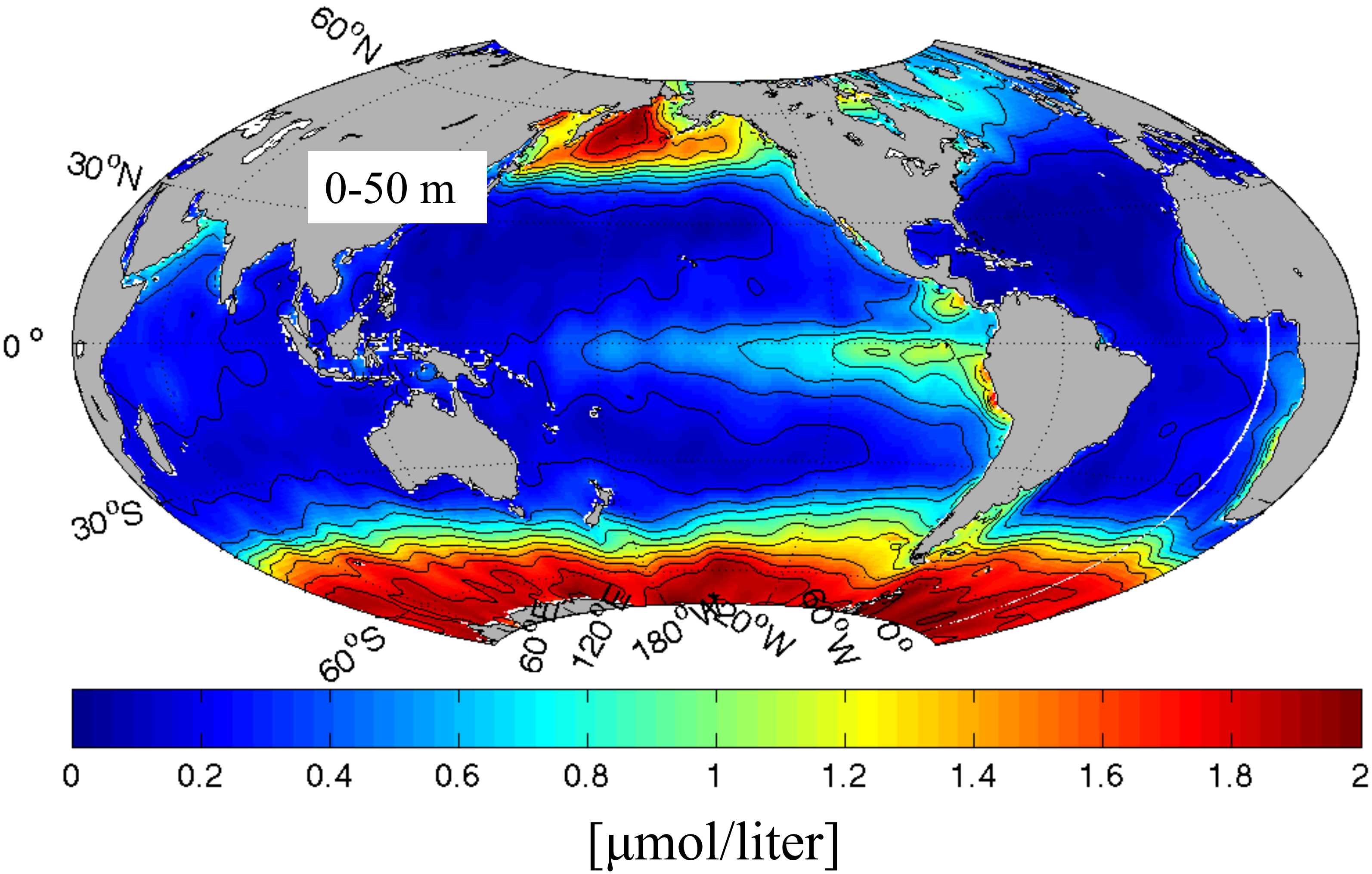
Preformed [PO_4^{3-}] (carried in the water from the surface)

Regenerated [PO_4^{3-}] (produced from degradation of sinking organic matter)

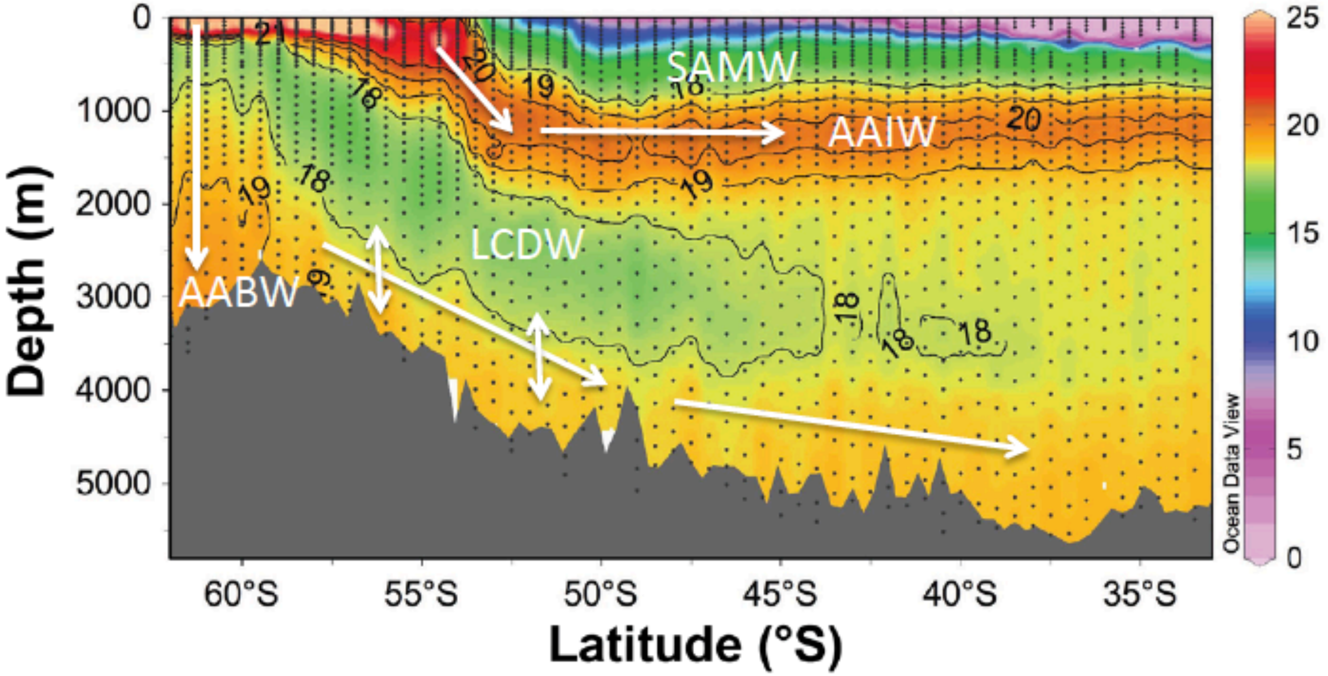


Sarmiento and Gruber, 2006

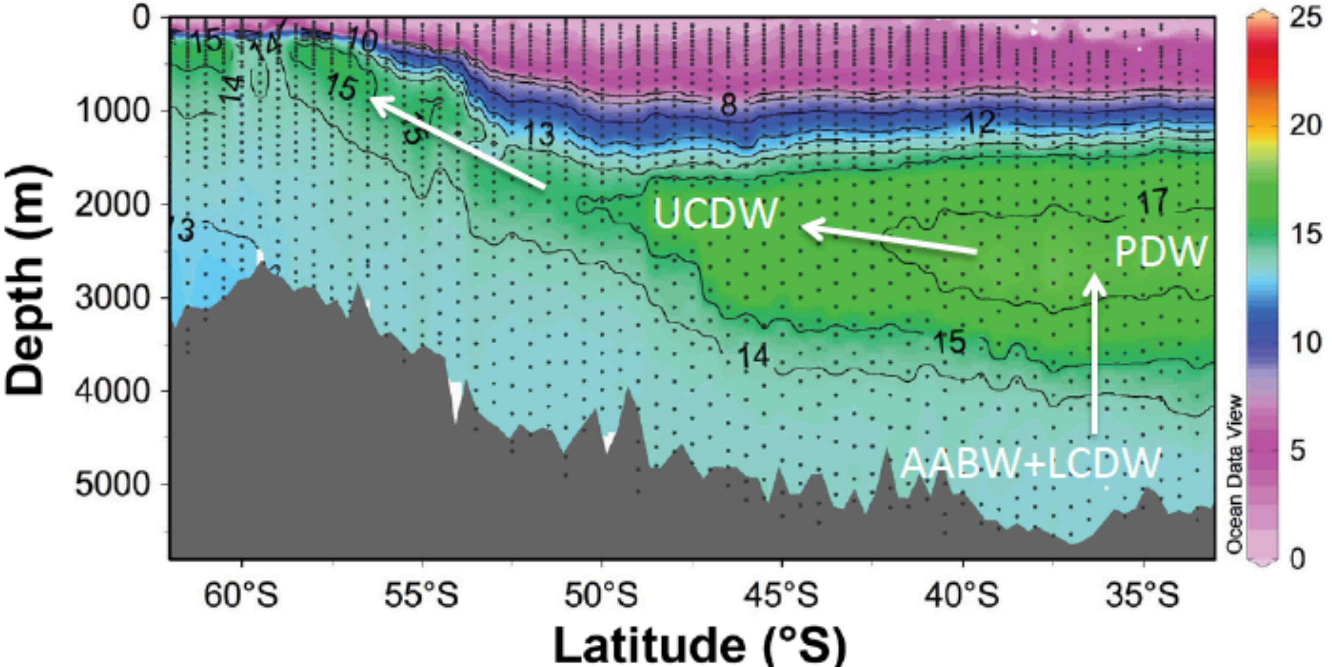
Annual average surface phosphate



Annual mean PO_4 [mmol/m^3] in the upper 50 m, from World Ocean Atlas [2005]. In most of the ocean, nutrients are extremely scarce because they have been consumed, limiting further photosynthesis. Exceptions are regions of strong vertical exchange with the remineralized subsurface reservoirs, or insufficient sunlight or micronutrients (e.g., dust).



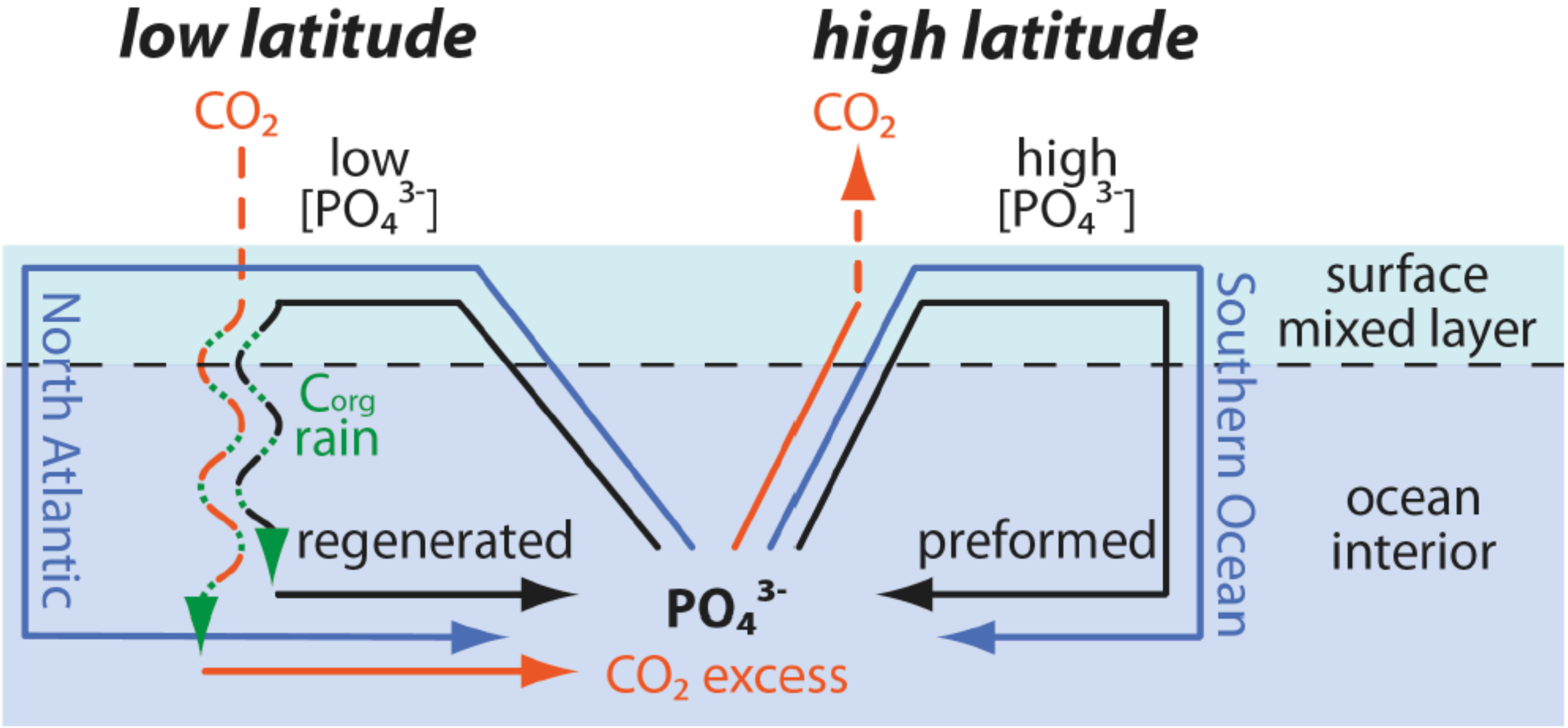
preformed $[NO_3^-]$ (μmol/kg)



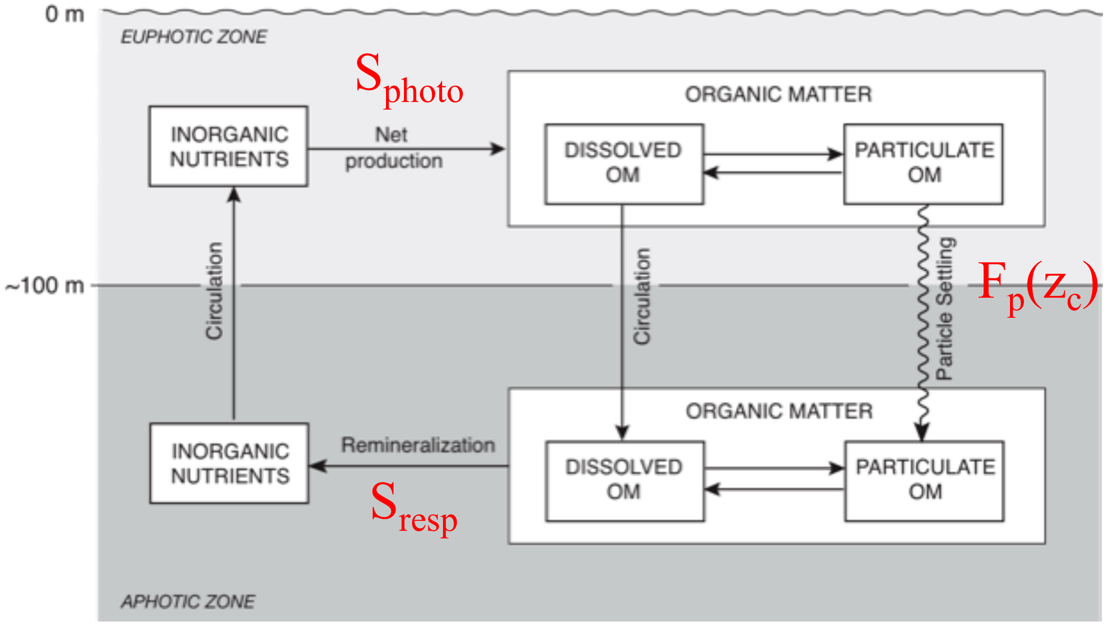
regenerated $[NO_3^-]$ (μmol/kg)

WOCE P16S data

Southern Ocean: leak in the biological pump



Biogeochemical Models



$$S_{photo} = \max\left\{\frac{P_{obs} - P}{\tau}, 0\right\}$$

$$F_p(z_c) = (1 - \phi_{DOM}) \int_0^{z_c} S_{photo}\,dz \quad \phi_{DOM} \sim 0.7$$

$$F_p(z) = F_p(z_c)\left(\frac{z_c}{z}\right)^b, \; b \sim 1$$

$$S_{resp}^{DOM} = \kappa \cdot DOP, \; \kappa \sim 2yr^{-1}$$

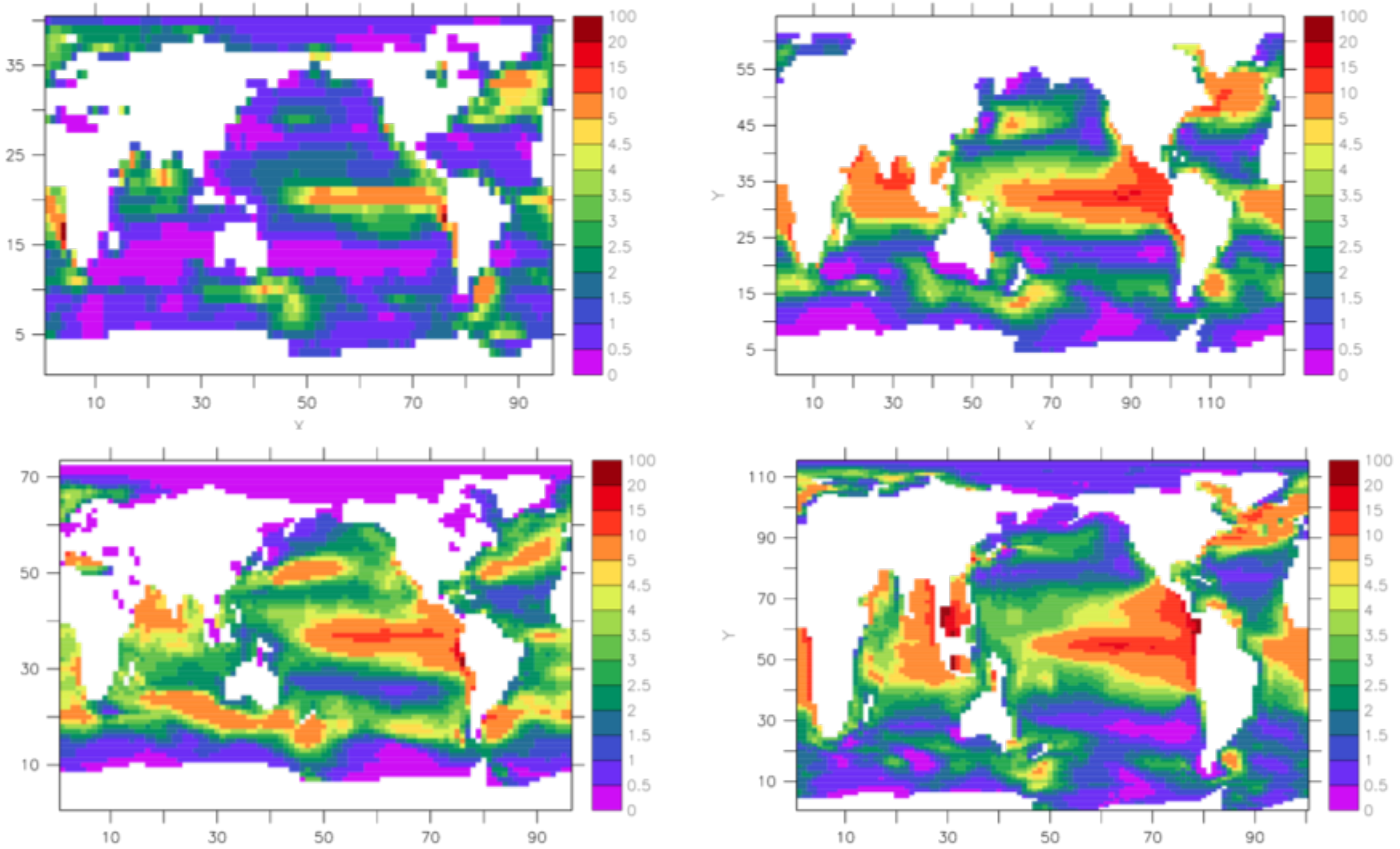
$$S_{resp}^{POM} = \frac{\partial F}{\partial z}$$

$$\phi_{DOM} + \phi_{POM} = 1$$

$$\frac{D(PO_4)}{Dt} = -S_{photo} + S_{resp}^{POM} + S_{resp}^{DOM}, \qquad \frac{D(DOP)}{Dt} = \phi_{DOM} S_{photo} - S_{resp}^{DOM}$$

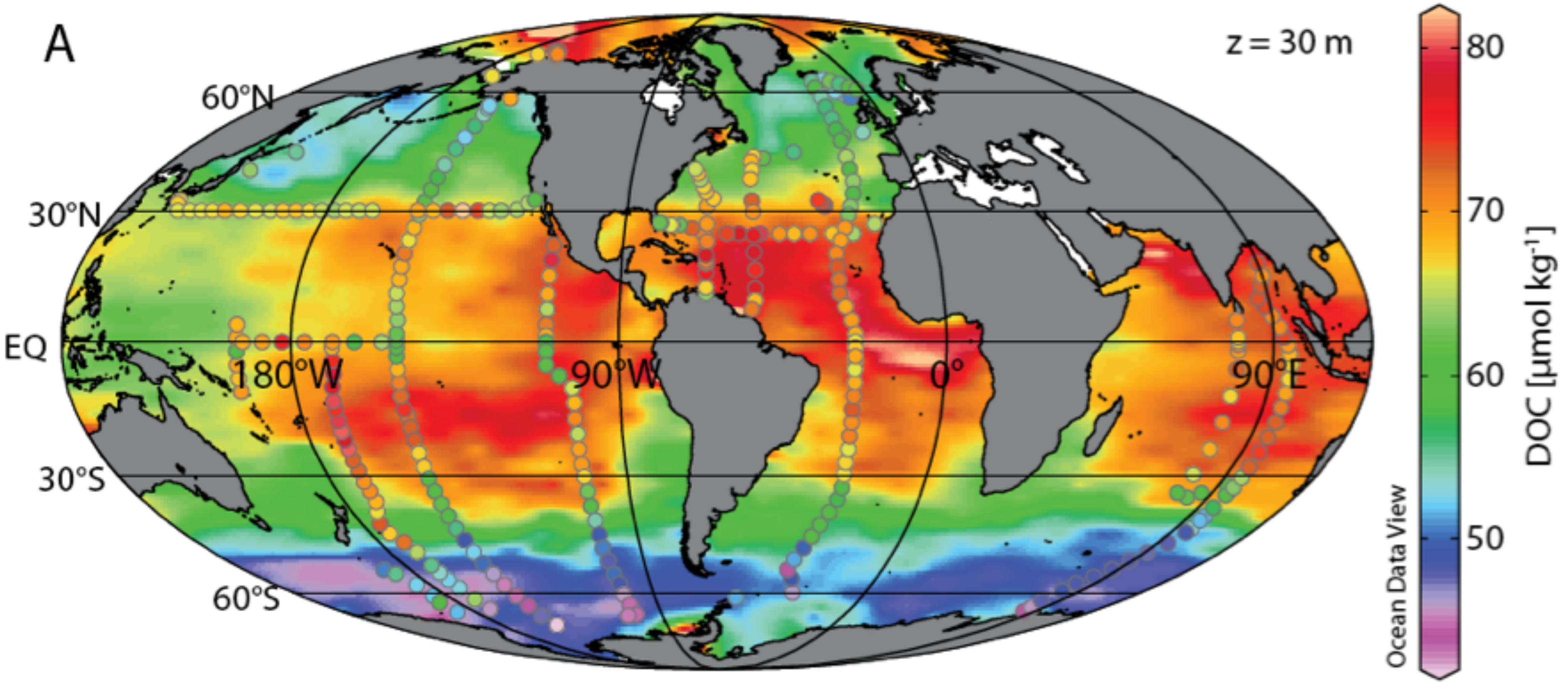
Diagram of a simple biogeochemical model (here for P) that uses observed nutrient distributions (P_{obs}) to infer hard-to-observe rates of biological processes (S_{photo}, S_{resp}) and particle fluxes, $F_p(z_c)$, with z_c the base of the euphotic zone. Some OGCMS have much more sophisticated models.

Particle (POM)) Export



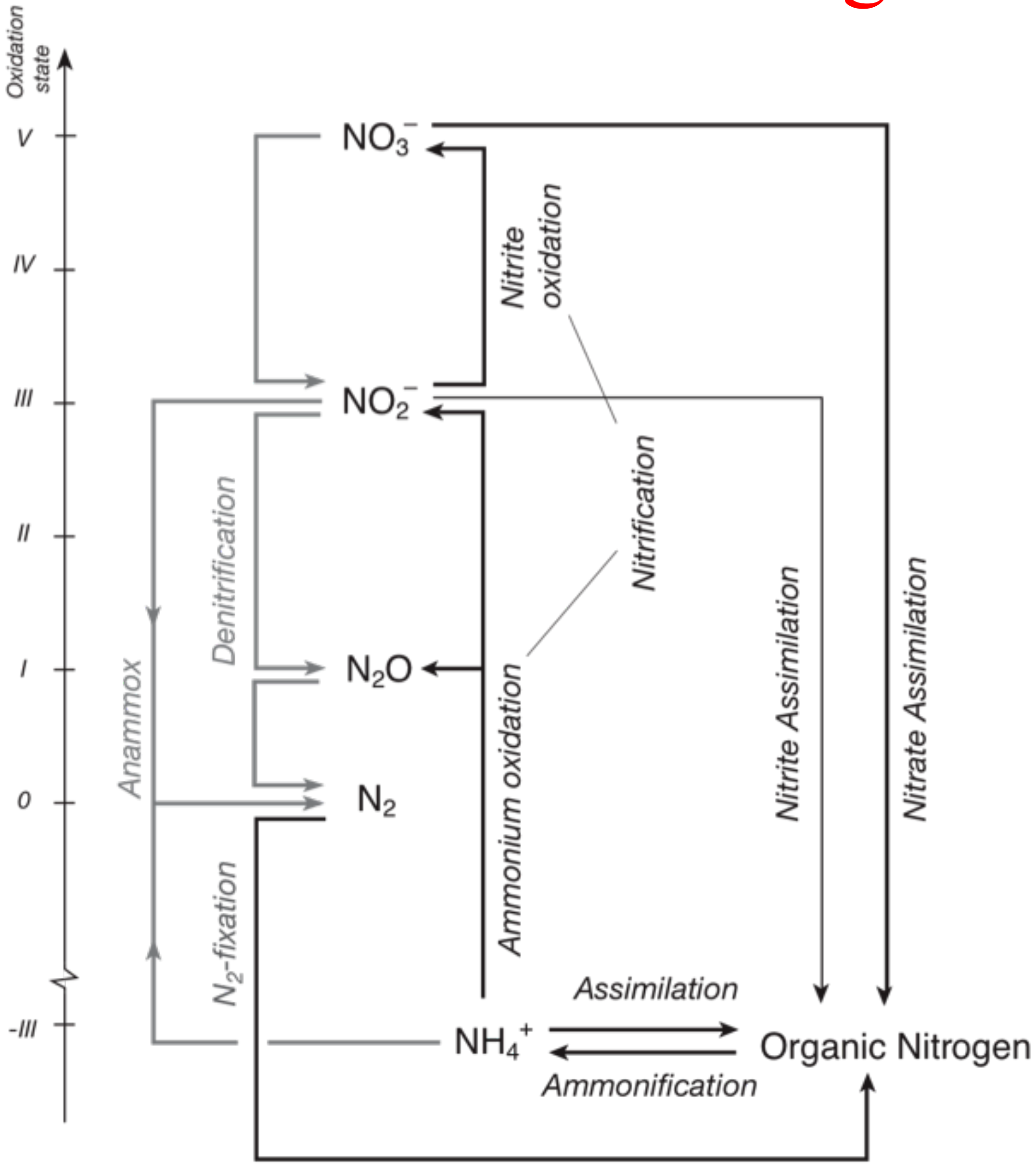
Flux F_p of POM (mol C/m2/yr) out of the surface ocean (75m), from four OGCMs (Princeton, MIT, NCAR, Hadley Center). Globally integrated values are 5-15 GtC/yr. [1 Gt = 1 Pg] An additional ~ 2 GtC is transported to the deep ocean as dissolved organic carbon. Spatial pattern of export can be used to estimate infer primary productivity (fueled by new nutrients into the euphotic zone) because the two roughly balance. Model differences in F_p are mainly due to circulation differences in nutrient supply.

Surface DOC



Distributions of dissolved organic carbon (DOC ; µmol/kg) at 30 m. Meridional and zonal lines of data are observed values, while the background field is modeled; notice moderate model-data differences where they overlap. DOC is mainly the waste products of biology, not the same as abundance (biomass; e.g., Chl) or growth (productivity). Low subpolar DOC is partly rapid vertical exchange with interior water with high DIC, but is also lack of iron for growth (in south).

The Nitrogen Cycle



- Several bioavailable forms of N (mostly NO_3). Vast reservoir of N_2 is nearly inert.

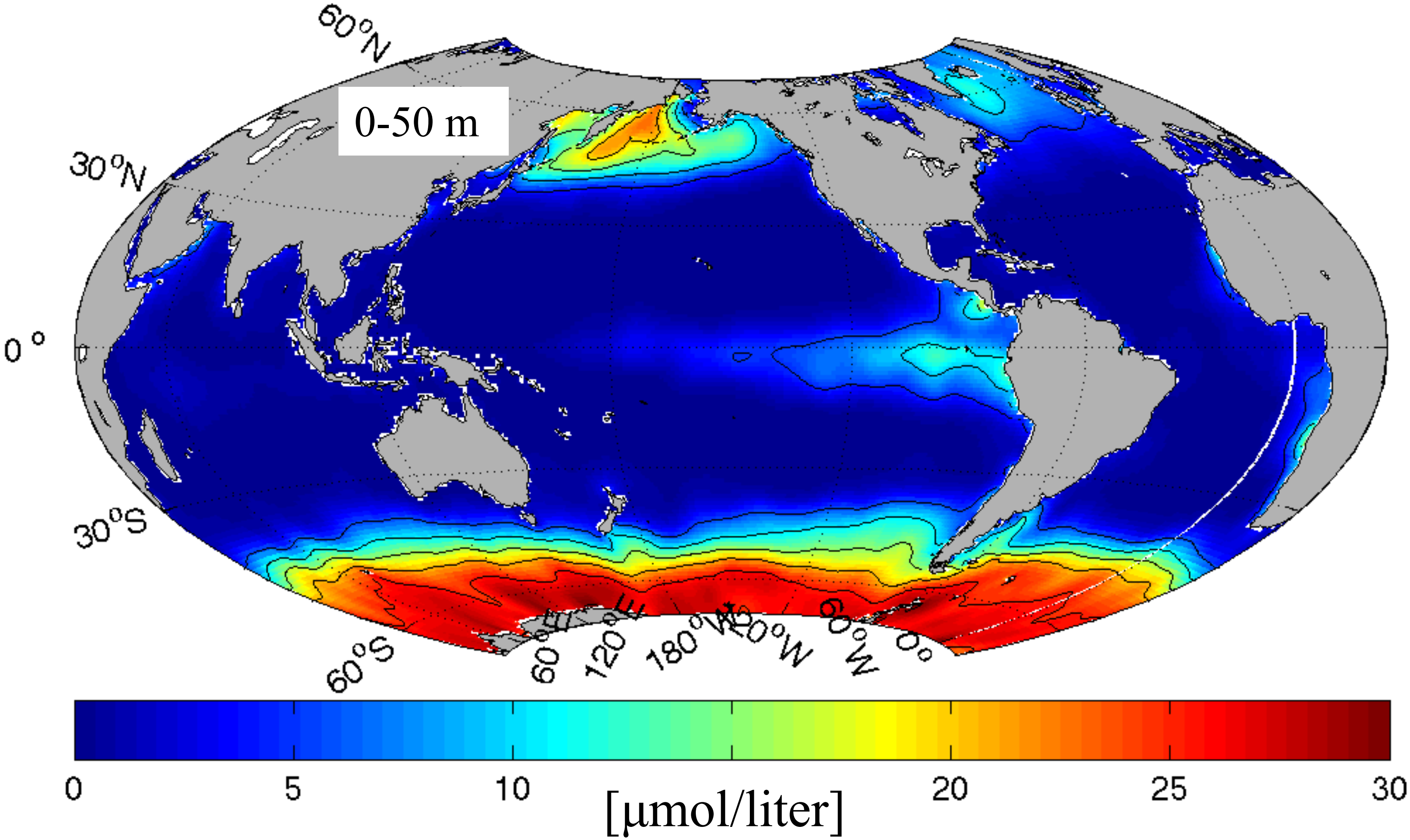
- N_2 can be converted to bioavailable N (i.e., fixed) by specialized organisms (diazotrophs), unlike other nutrients.

- Biological sources of N are much larger than non-biological sources (atmosphere, rivers), apart from agricultural eutrification locally.

- N_2O (greenhouse gas) is produced in reactions, emitted to atmosphere, by denitrification where O_2 is low or in sediments.

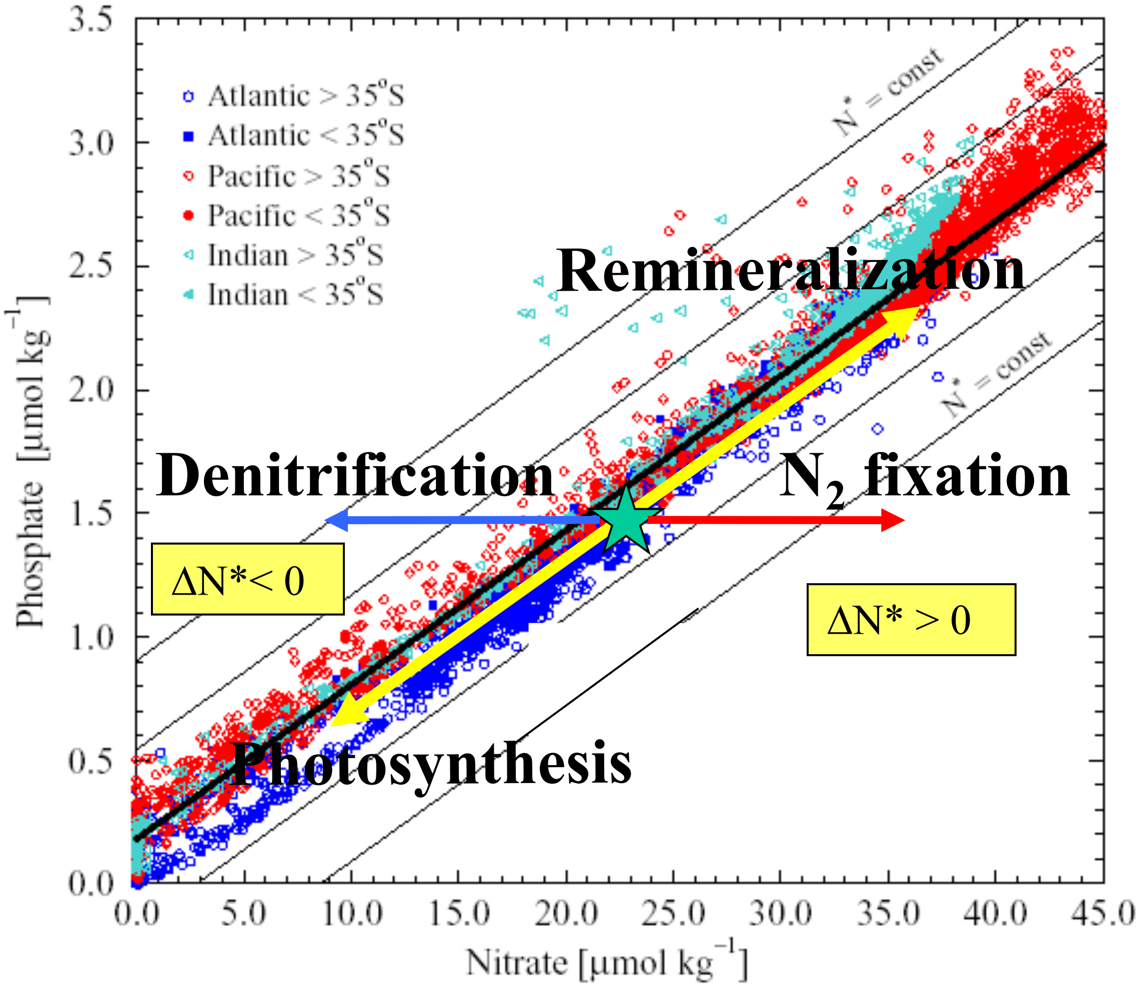
- 'Residence time" (inventory/input rate) of N is very short, ~2000 yrs making it susceptible to large changes (cf., $\tau_{PO4} \sim$ 50,000 yrs). This is slightly shorter than the global mixing time (maximum age).

Annual average surface nitrate



Annual mean nitrate (NO_3 [$mmol/m^3$]) in the upper 50 m, from World Ocean Atlas [2005]. Note very close correlation to PO_4 (slide 18), but generally lower values relative to biomass N:P requirements (i.e. $r_{N:P}=16$), implying a nitrate limitation to growth.

Nitrogen vs. Phosphorus



Starting from:

$$\frac{DPO_4}{Dt} = S_{photo}(PO_4) + S_{resp}(PO_4)$$

$$\frac{DNO_3}{Dt} = S_{photo}(NO_3) + S_{resp}(NO_3) + \ldots$$
$$+ S_{Nfix} - S_{denit}$$

Define:

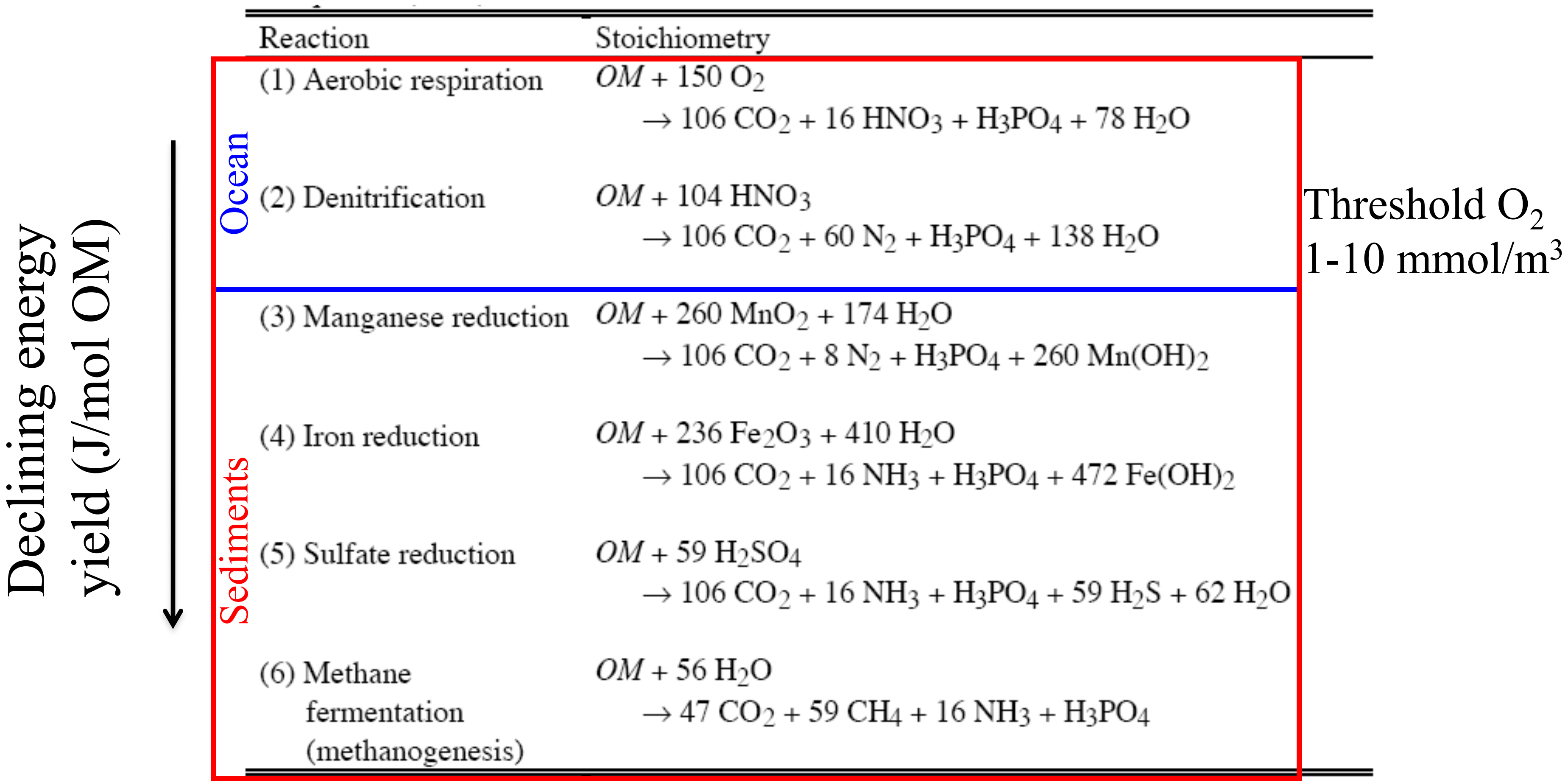
$$N^* = NO_3 - r_{N:P} PO_4$$

Then:

$$\frac{DN^*}{Dt} = S_{Nfix} - S_{deni}$$

Global correlation between NO_3 and PO_4. Slope is similar to the Redfield ratio for biomass ($r_{N:P}$=16) indicating dominance of photosynthesis/remineralization. Small deviations from the 16:1 covariation, are caused by denitrification (S_{denit}) and N_2 fixation (S_{Nfix}) and can be quantified with the tracer N*. The geographical differences are real but secondary to the N-P coupling in the equation of sea life.

Oxidation Reactions

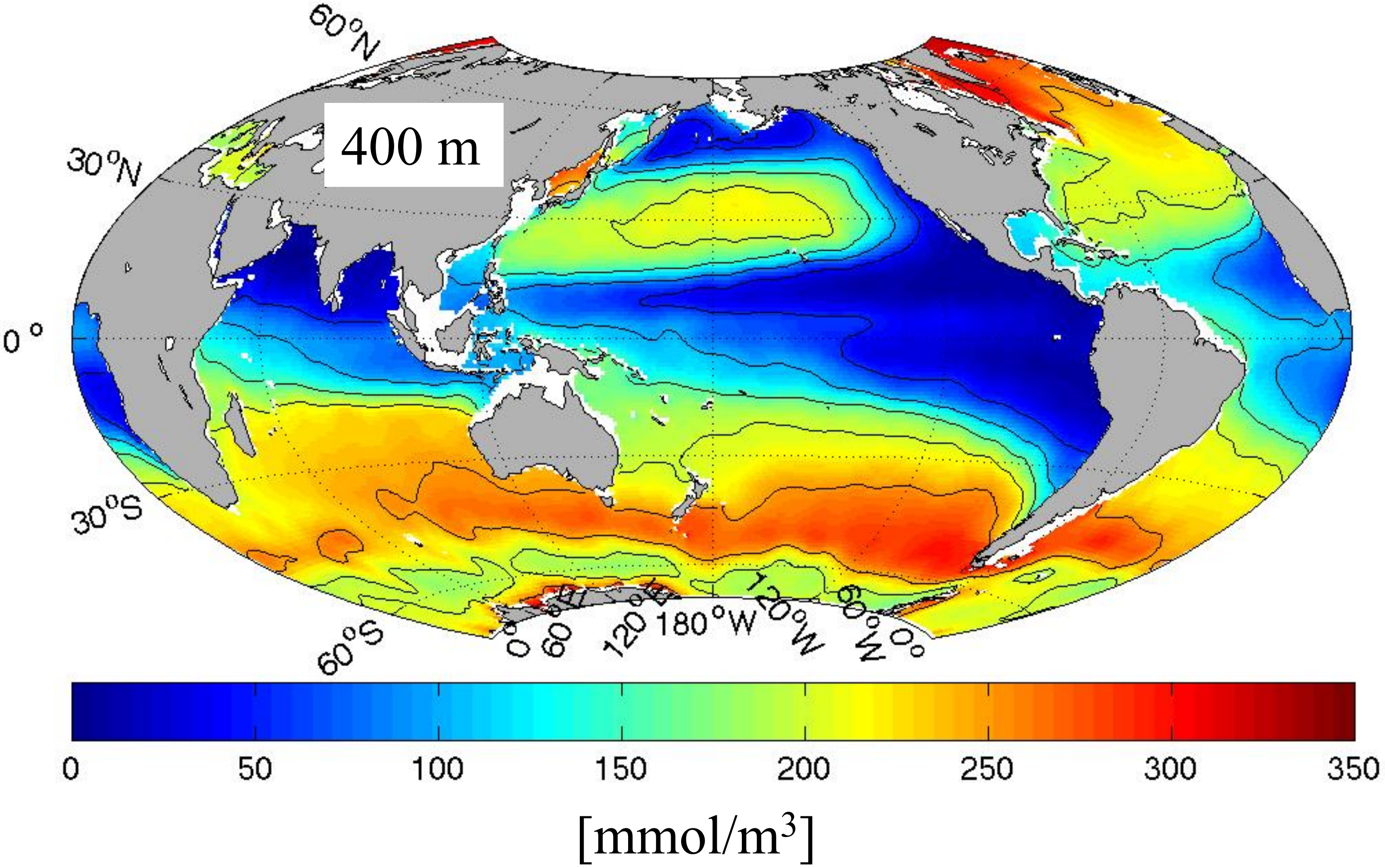


Reaction	Stoichiometry
(1) Aerobic respiration	$OM + 150\ O_2$ $\rightarrow 106\ CO_2 + 16\ HNO_3 + H_3PO_4 + 78\ H_2O$
(2) Denitrification	$OM + 104\ HNO_3$ $\rightarrow 106\ CO_2 + 60\ N_2 + H_3PO_4 + 138\ H_2O$
(3) Manganese reduction	$OM + 260\ MnO_2 + 174\ H_2O$ $\rightarrow 106\ CO_2 + 8\ N_2 + H_3PO_4 + 260\ Mn(OH)_2$
(4) Iron reduction	$OM + 236\ Fe_2O_3 + 410\ H_2O$ $\rightarrow 106\ CO_2 + 16\ NH_3 + H_3PO_4 + 472\ Fe(OH)_2$
(5) Sulfate reduction	$OM + 59\ H_2SO_4$ $\rightarrow 106\ CO_2 + 16\ NH_3 + H_3PO_4 + 59\ H_2S + 62\ H_2O$
(6) Methane fermentation (methanogenesis)	$OM + 56\ H_2O$ $\rightarrow 47\ CO_2 + 59\ CH_4 + 16\ NH_3 + H_3PO_4$

Threshold O_2
1-10 $mmol/m^3$

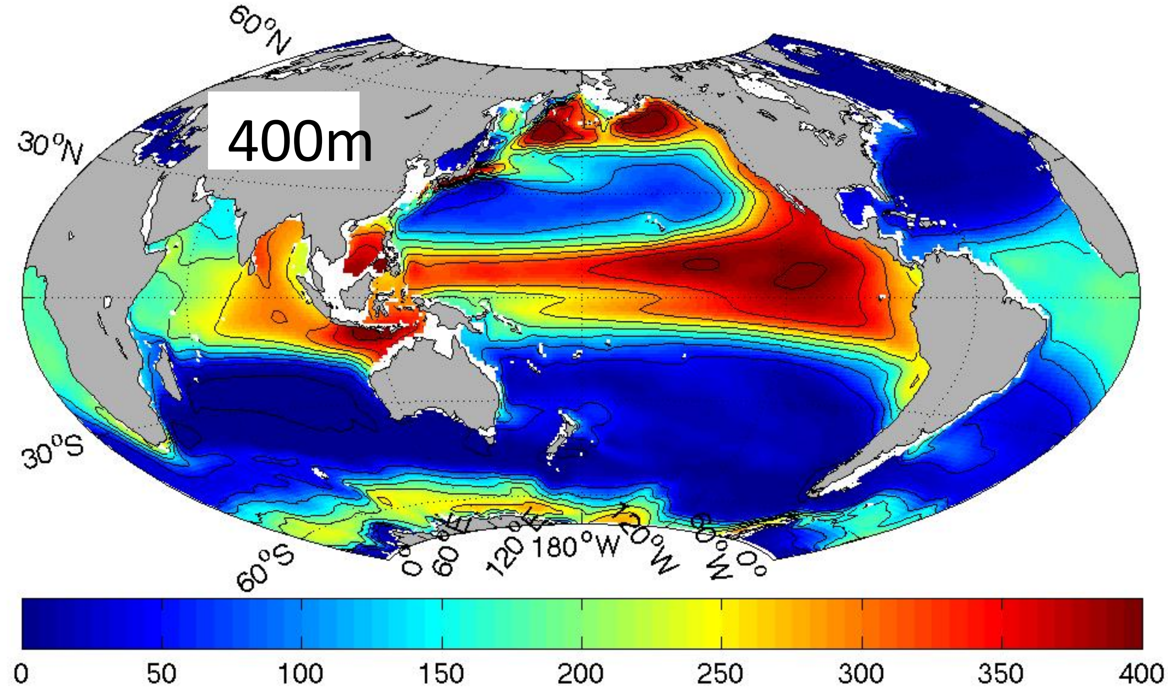
Sequence of reactions for oxidizing organic matter, ranked by energy of reaction. At low O_2 levels (<10 $mmol/m^3$), respiration proceeds via denitrification, a process that removes NO_3 from the ocean, and accounts for the N limitation of photosynthesis. In current ocean, subsequent reactions (3-6) are confined to sediments. Redfield ratio indicates dominance of aerobic respiration in seawater.

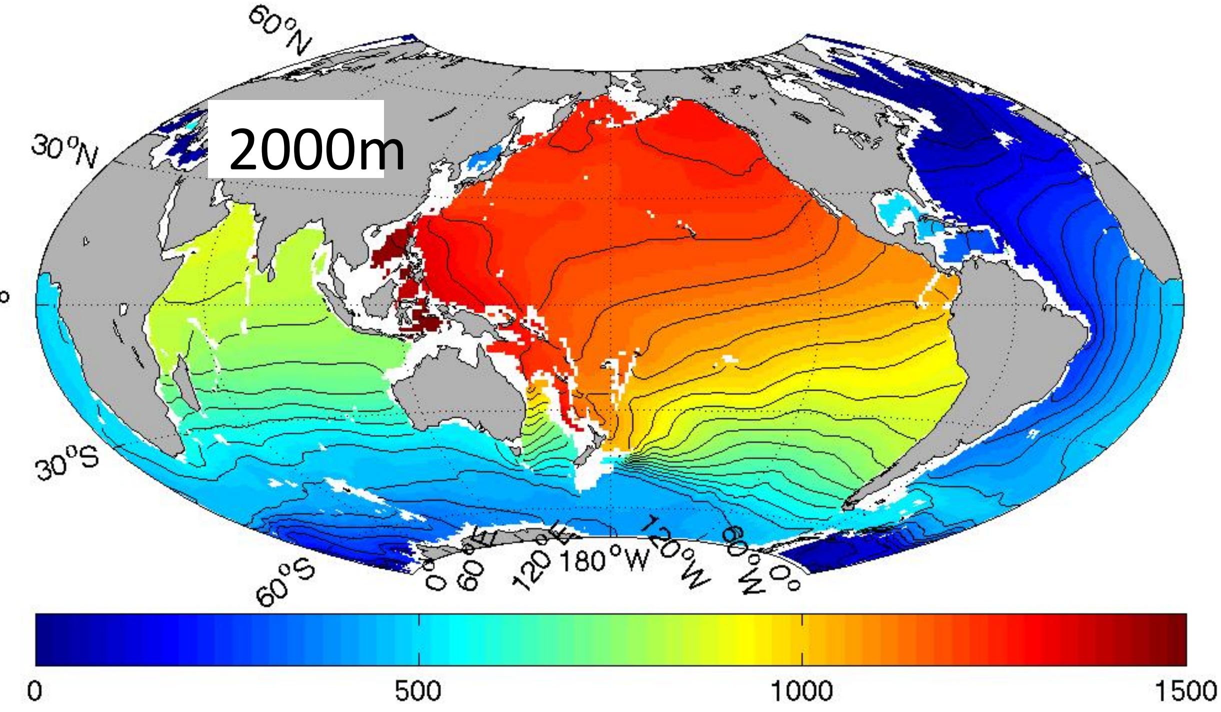
Oceanic Oxygen in the Interior



Annual mean oxygen, O_2 [mmol/m^3], in the thermocline (400 m), from World Ocean Atlas [2005]. Respiration leads to anoxic conditions in the tropical Pacific and Indian Oceans, where waters are old and underlying high productivity surface waters with local respiration of high POM "marine snow".

Ocean "Age"





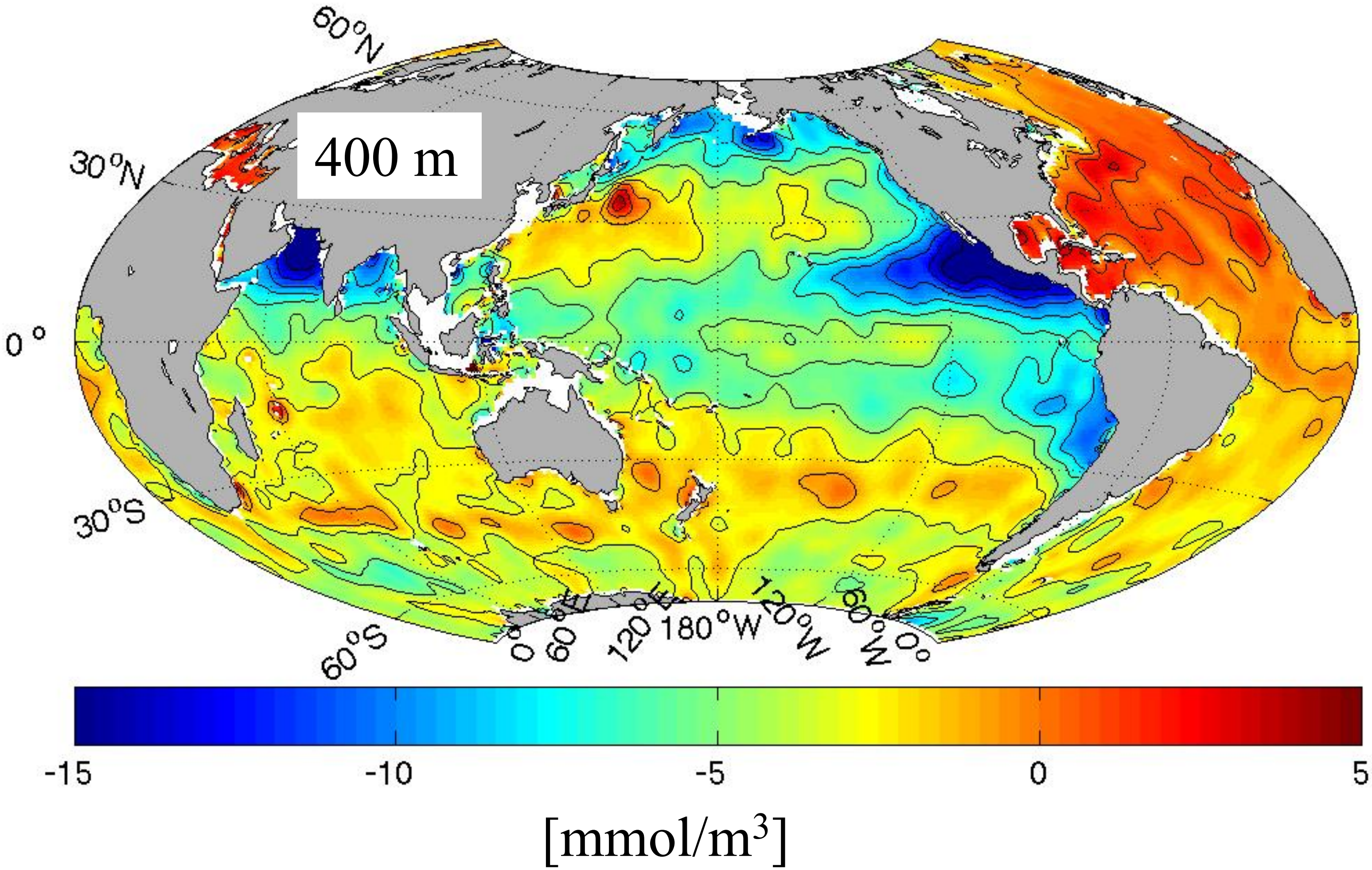
The ideal age tracer:

$$\frac{D\tau}{Dt} = 1 \qquad \tau(z=0) = 0$$

computed from an ocean model (ECCO2). Units: years. In model evaluations, there is also age mixing.

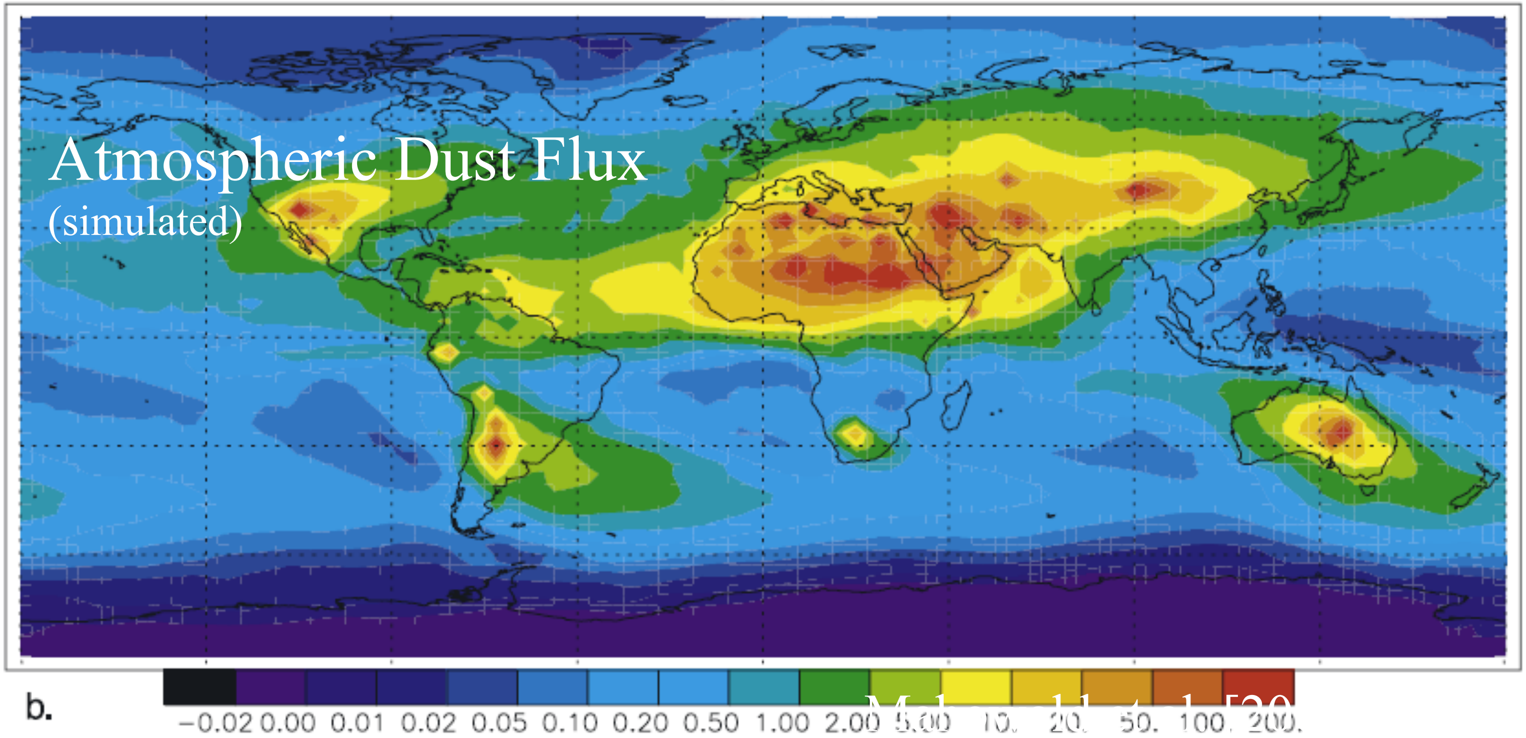
Note correspondence between ideal age, O_2. and empirical CFC-11 age in the thermocline (Circulation lecture).

Nitrogen loss



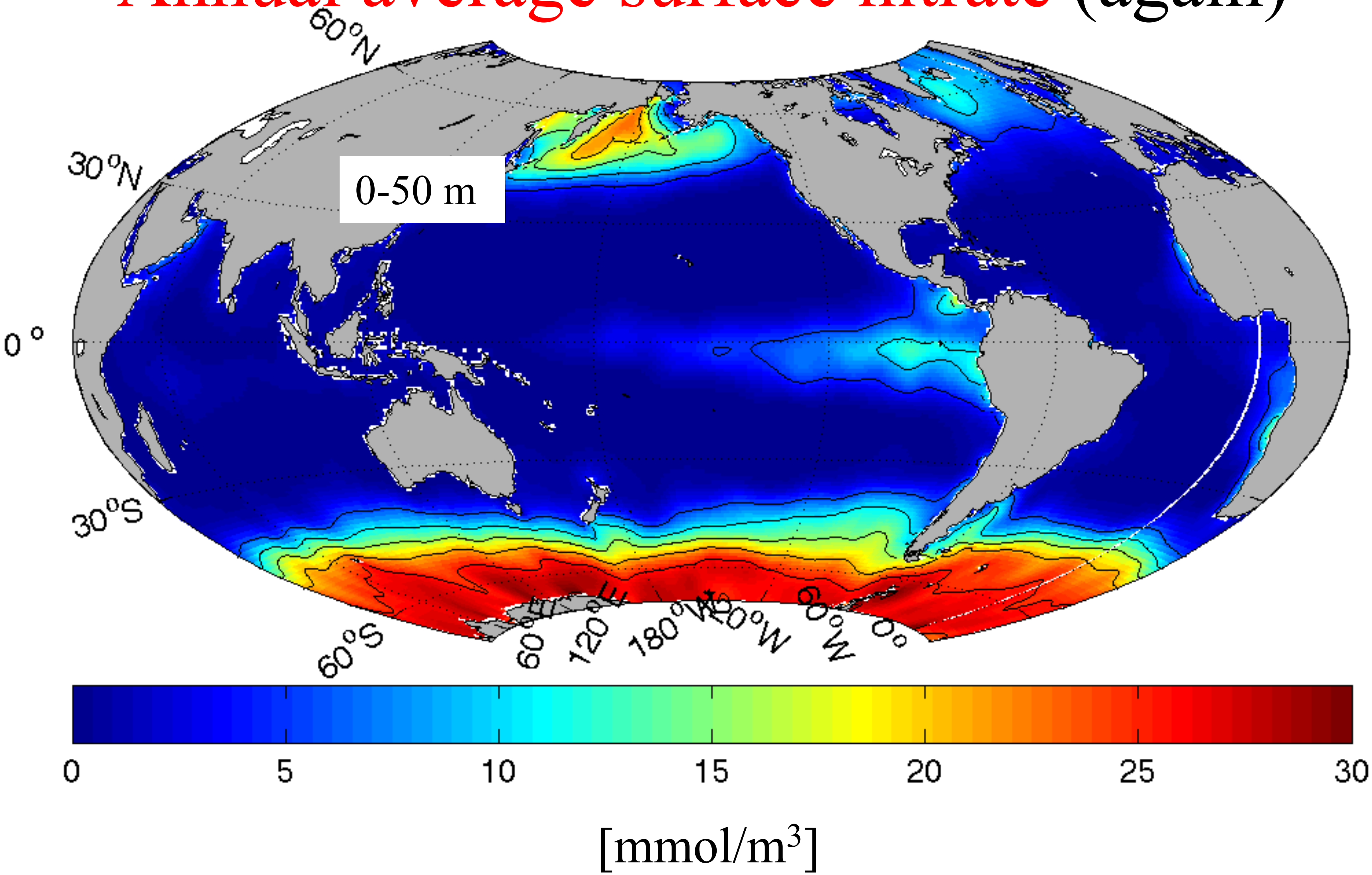
Annual mean nitrate deficit (N* [mmol/m^3]) in the thermocline (400 m), from World Ocean Atlas [2005]. Largest negative values are found in low-O_2 waters with denitrification where N replaces O in respiration. Highest values found in Atlantic thermocline with higher O_2 and more N_2 fixation. This is non-Redfield.

Iron input via dust



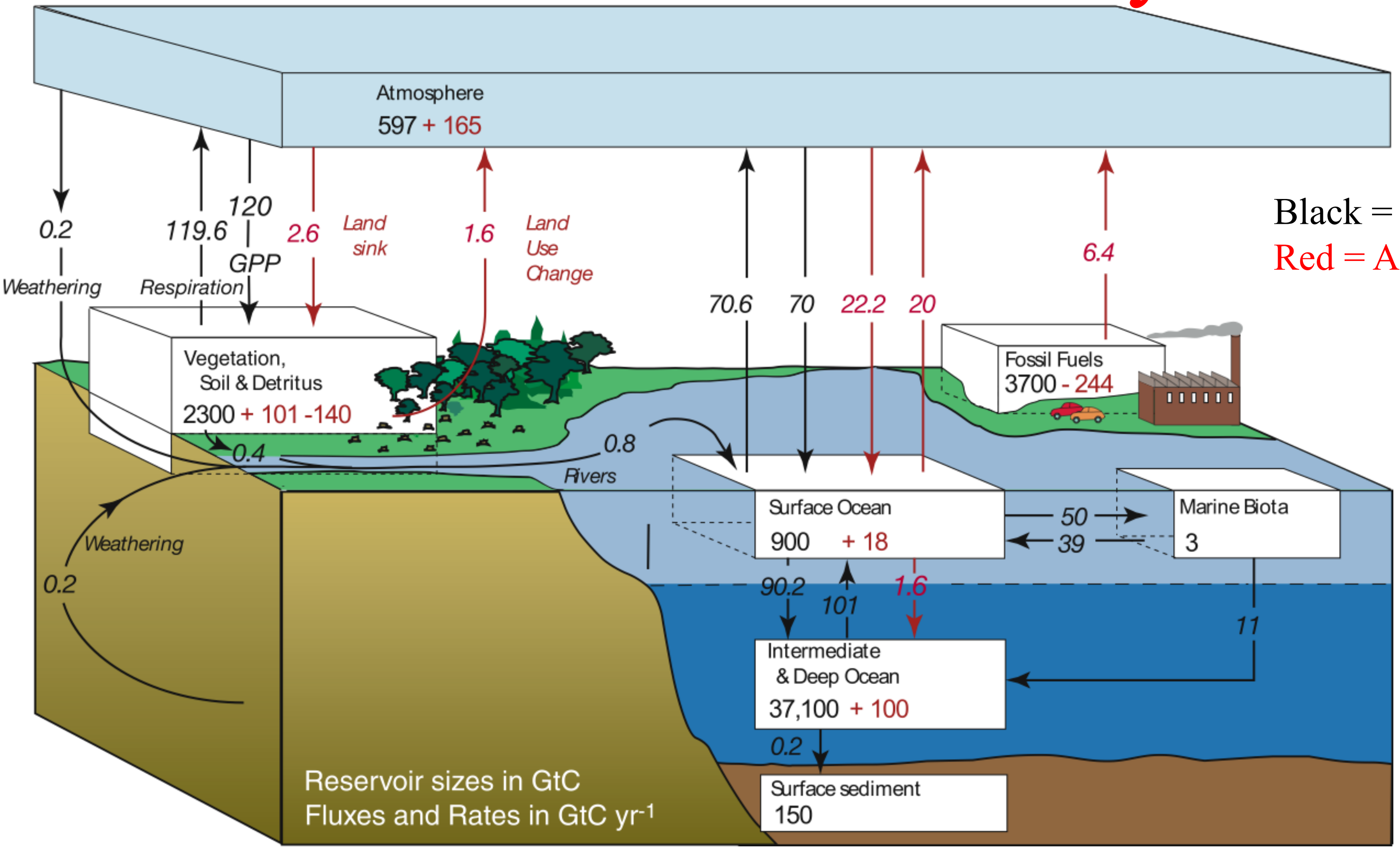
Rate of dust deposition (g/m^2/yr) estimated by atmospheric transport and land surface models (note log scale). Continental dust is a major source of iron and other micronutrients to the ocean surface and may limit many biochemical processes, including N_2 fixation and overall productivity. Notice low deposition in tropical Pacific vs. Atlantic, and in polar regions, especially near Antarctica. This causes HNLC (high nutrients, low chlorophyll) regimes.

Annual average surface nitrate (again)



Biological productivity is limited by available NO_3 throughout most of low-middle latitudes. What explains the incomplete consumption in other areas? …light, micro-nutrients, vertical exchange, gyre circulation, eddy stirring, … Ultimately the quantitative synthesis of these multiple influences can only be done with OGCMs.

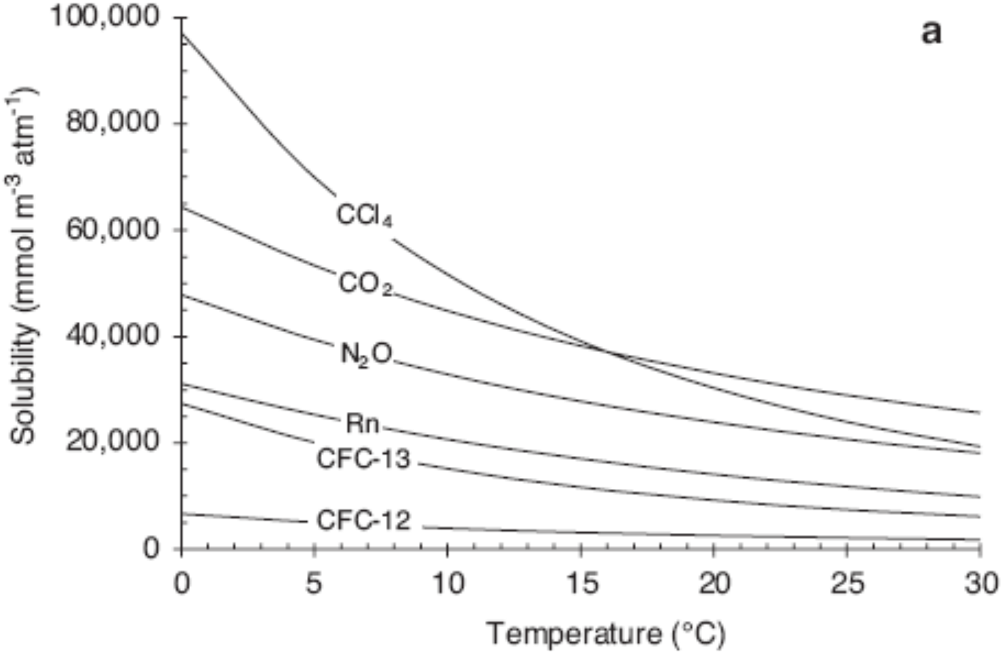
The Global Carbon Cycle



Black = Preindustrial
Red = Anthropogenic

What determines the partition of carbon between the atmosphere (~1%), ocean (>90%), and terrestrial biosphere (<10%)? The global carbon cycle for the 1990s, showing the main annual fluxes in GtC yr^{-1} : pre-industrial 'natural' fluxes in black and 'anthropogenic' fluxes in red (modified from Sarmiento and Gruber, 2006). Atmospheric carbon content and all cumulative fluxes since 1750 to 1994.

DIC: aqueous CO_2 Reactions



$$
\begin{aligned}
CO_{2\,(gas)} + H_2O &\Longleftrightarrow H_2CO_3^* \\
H_2CO_3^* &\Longleftrightarrow H^+ + HCO_3^- \\
HCO_3^- &\Longleftrightarrow H^+ + CO_3^{2-}
\end{aligned}
$$

$$
\begin{aligned}
K_0 &= \frac{[H_2CO_3^*]}{pCO_2} \\
K_1 &= \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]} \\
K_2 &= \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}
\end{aligned}
$$

Solubility of CO2 and other gases versus temperature (upper panel) and its subsequent reactions with water (lower), which produce three non-gaseous DIC species --- carbonic acid (H_2CO_3*), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}) --- in equilibrium reactions. The partition of C depends on pH (next slide). K_0 reflects Henry's Law for air-sea gas exchange. $CO_2^* = CO_2 + H_2CO_3^*$ is total dissolved CO2 in ocean.

Charge Balance in the Ocean:

The ocean is electrically neutral to a high degree => it has zero net charge; i.e.,

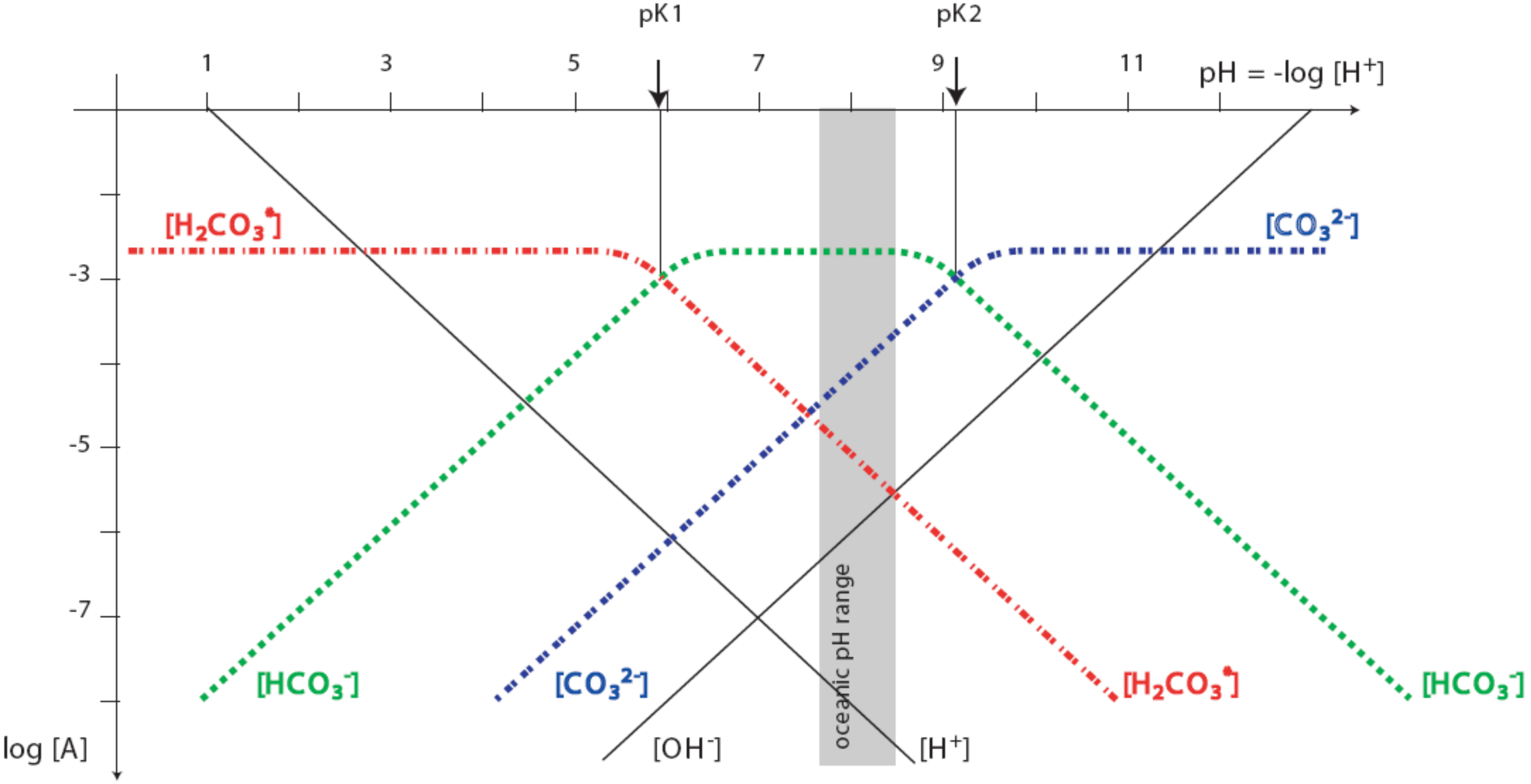
sum of cations (+ charge) – sum of anions (- charge) = 0.

pH = - log10([H+]) is a measure of acidity (less is more). The average pH in sea water is about 8.1 --- slightly basic or alkaline.

Alkalinity:

Alk = sum of charges (anions – cations) from strong electrolytes (highly ionized molecules) = - sum of charges from weak electrolytes (partially ionized molecules).

DIC Partitioning in Equilibrium



← **Acidic** **pH Scale** **Basic** →

Carbon speciation (log concentration) versus pH, for a fixed total DIC content. At more acidic (lower pH) conditions, CO$_2$ (i.e. H2CO3*) is dominant, whereas in basic water, carbonate CO$_3$ is dominant. Ocean is nearly neutral but slightly basic. As CO$_2$ is added, H+ increases (pH lowers) & greater fraction of C atoms present as CO$_2$, ocean becomes more acidic. CO$_2$* is only about 1% of total DIC => large C storage in ocean.

Measured Quantities

To completely specify the chemical speciation of C in seawater, two measurements are needed. Total inorganic carbon concentration (DIC) and pH would be a natural choice, but for practical experimental reasons, Alkalinity is used instead of pH.

Dissolved Inorganic Carbon (DIC) = all the inorganic C molecules

$$\begin{array}{ccccc} DIC & = & [H_2CO_3^*] & + & \boxed{\begin{array}{ccc} [HCO_3^-] & + & [CO_3^{2-}] \\ 88.6\% & & 10.9\% \end{array}} \\ & = & 0.5\% & & \end{array}$$

Alkalinity (Alk) = net charge of all species effected by C reactions

$$\begin{array}{ccccccccc} Alk & = & \boxed{\begin{array}{ccc} [HCO_3^-] & + & 2 \ast [CO_3^{2-}] \\ 76.8\% & & 18.8\% \end{array}} & + & [OH^-] & - & [H^+] & + & [B(OH)_4^-] \\ & & & & & 0.2\% & & & 4.2\% \end{array}$$

(borate)

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

Concept: $\mathrm{CO_2}$ in the ocean is highly buffered; *i.e.*, for any air-sea gas flux of $\mathrm{CO_2}$, relatively little change occurs in $[CO_2^*]$.

$[CO_2^*]$ is only about 0.6% of DIC in the ocean at essentially every location.

This is a negative chemical feedback.

This implies that once a disequilibrium arises in $\mathrm{pCO_2}$ between the atmosphere and surface ocean, it will persist for a long time and be removed only slowly ($\Delta t \sim 1$ yr) after a large exchange of $\mathrm{CO_2}$ has occurred.

Influences on pCO_2: Downward C pumps: solubility, soft-tissue (organic), & carbonate

=> Alk increases with depth (and DIC usually does too).

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

K_0: Solubility of CO_2
K_1, K_2: Dissociation constants

K are functions of T and S, but K_2/K_1 only weakly so.

Depends on biology (DOC, POC) and gas exchange

Depends on biology (Calcium carbonate in shells):

Increasing acidity in global change reduces Alk and depletes shells.

Simplified Model of Equilibrium Inorganic Carbon Chemistry

Compact notation: $C_1 = [CO_2^*],\ C_2 = [HCO_3^-],\ C_3 = [CO_3^{2-}],\ H = [H^+],\ D = DIC,\ A = Alk_C \approx Alk_T,\ P = pH = \log_{10}[H^+],\ pC = pCO_2$.

$$\begin{aligned} D &= C_1 + C_2 + C_3 \,, \qquad A = C_2 + 2C_3 - H \\ C_1 = K_0\, pC \,, &\qquad K_1 C_1 = C_2\, H \,, \qquad K_2\, C_2 = C_3\, H \,. \end{aligned}$$

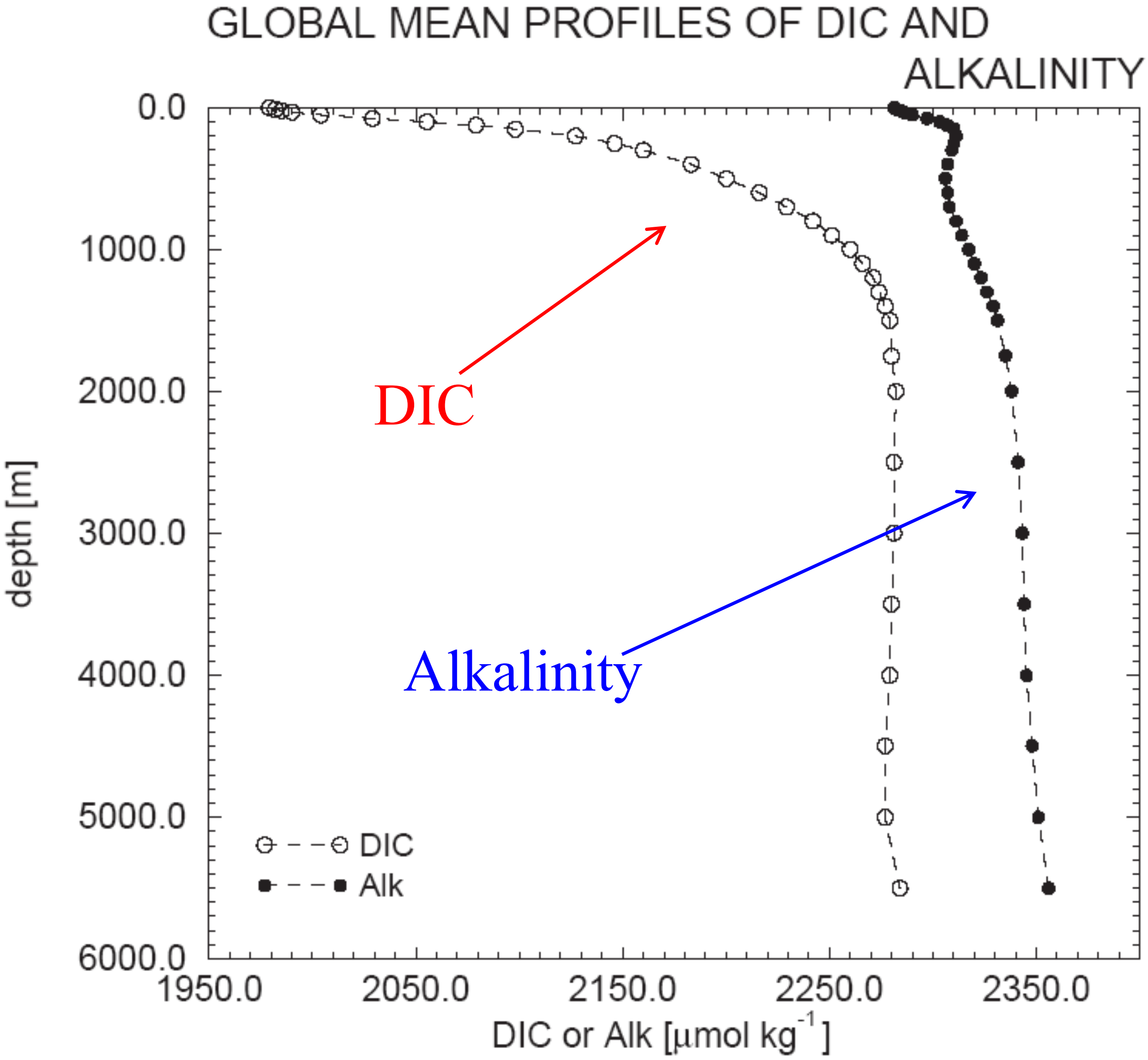
$\Rightarrow$ 5 equations, 3 rate constants, and 7 unknown concentrations. **Note:** this is not quite the same as WF, Box 6.3.

E.g., For given (K_0, K_1, K_2), D, and A, what is P?

E.g., For given (K_0, K_1, K_2) and A, how do D and P change with a change in pC?

Concepts: The rate constants are functions of T and S, biogeochemistry provides sources and sinks for C_1 and C_3, and pC is highly variable with implications for air-sea CO_2 flux.

Carbon Pumps: surface vs. deep

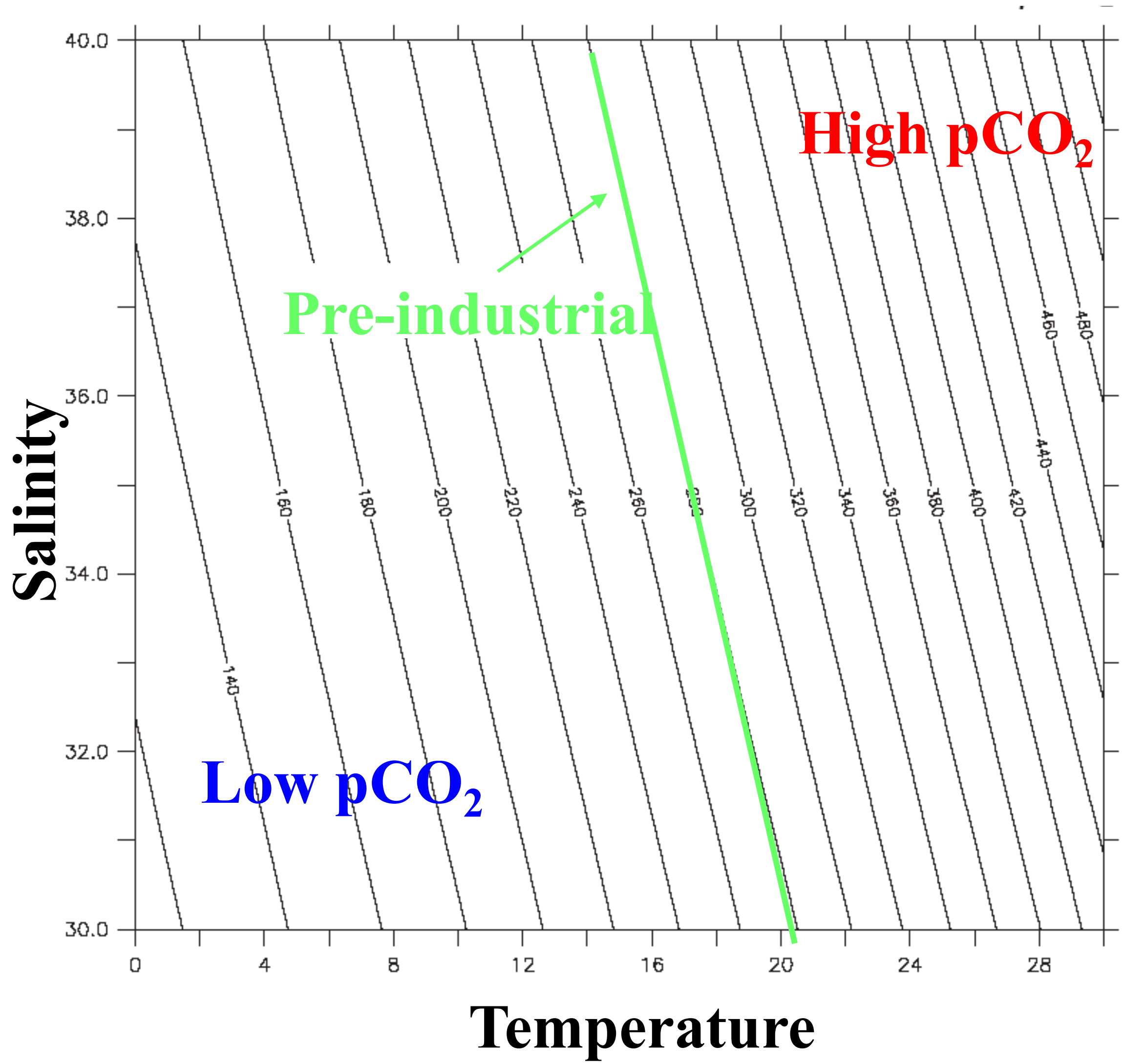


Carbon storage in deep ocean is enhanced by:

1) Cold temperatures (solubility pump, DIC)
2) Sinking organic material (organic pump, DIC)
3) Sinking $CaCO_3$ (carbonate pump, Alk)

The organic pump is largest. The carbonate pump is smallest, but has a counterintuitive effect; by reducing Alkalinity, it raises the pCO2 of the surface ocean, which then escapes to the atmosphere.

pCO$_2$ vs Temperature, Salinity

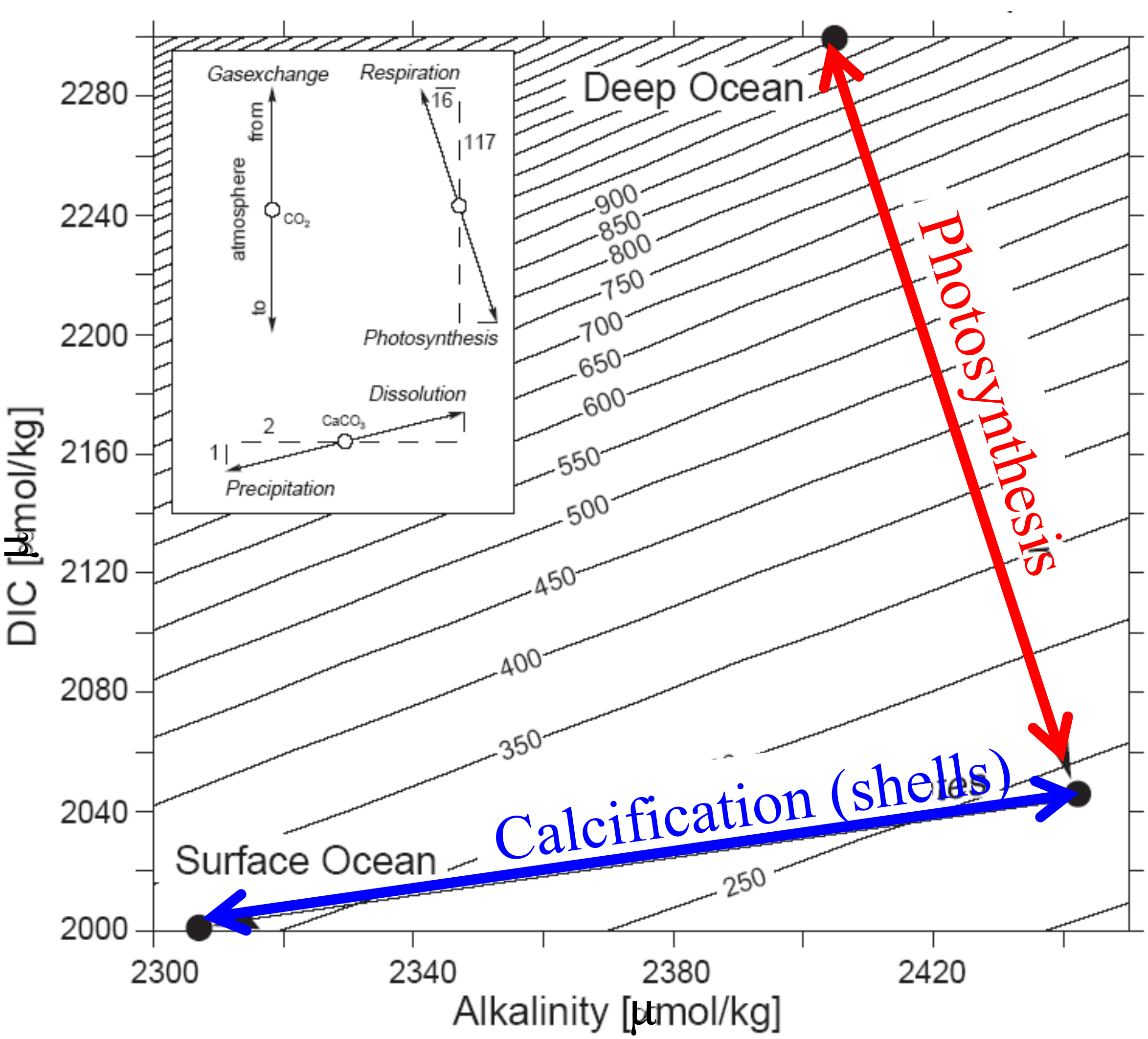


Dependence of pCO$_2$ [μ atm] on temperature and salinity (DIC and Alk held constant):

$$\frac{\partial \ln(pCO_2)}{\partial T} \approx 4.2\% \, C^{-1}$$

$$\frac{\partial \ln(pCO_2)}{\partial \ln(S)} \approx 1$$

pCO$_2$ vs DIC, Alkalinity



(~pH)

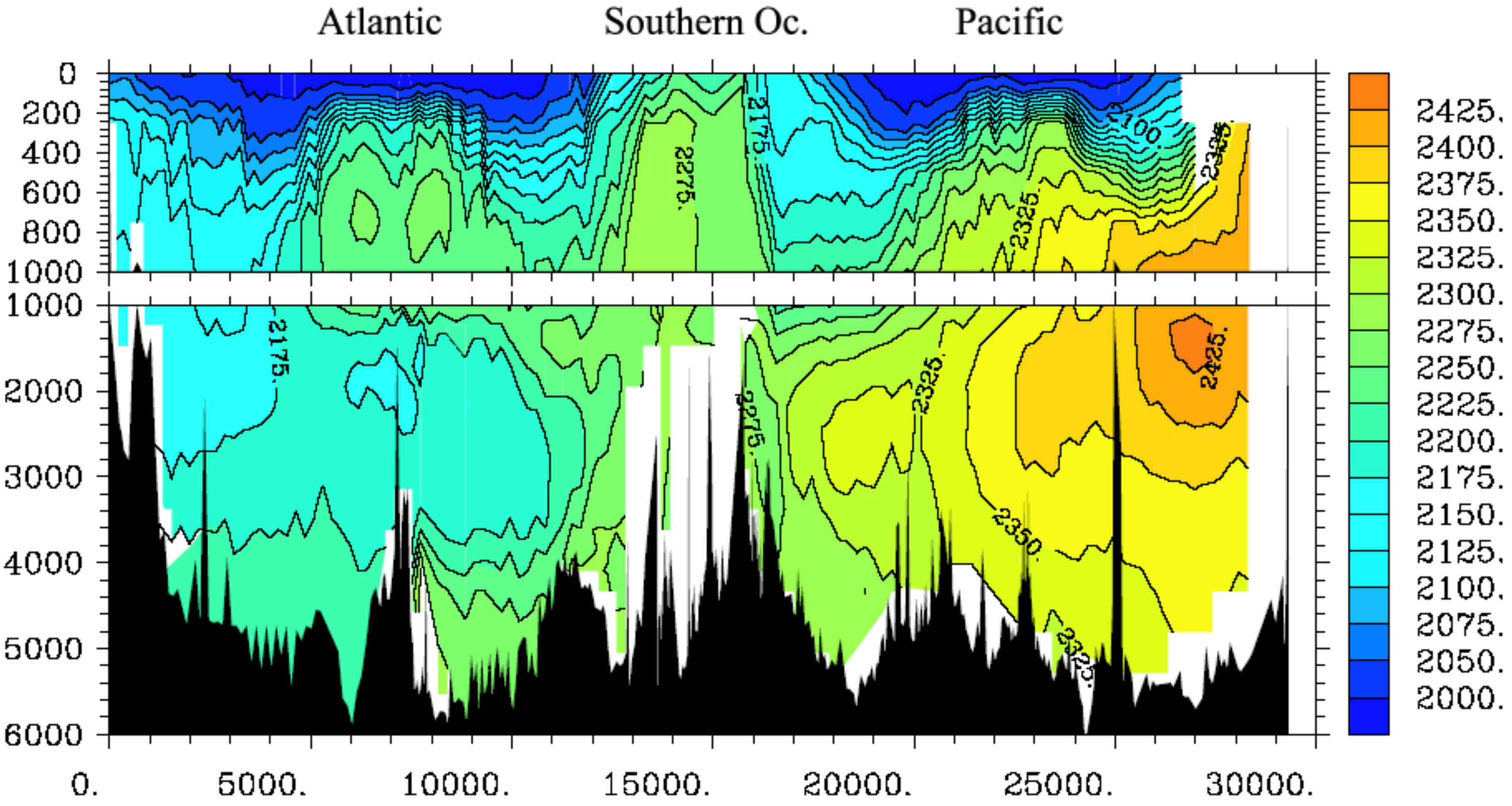
Dependence of pCO$_2$ [μ atm] on DIC and Alk (T and S held constant):

$$\frac{\partial \ln(pCO_2)}{\partial \ln(DIC)} \approx 10$$

This quantity (known as the buffer or "Revelle" factor) gives the fractional change in pCO2 required to raise DIC., which depends on pH.

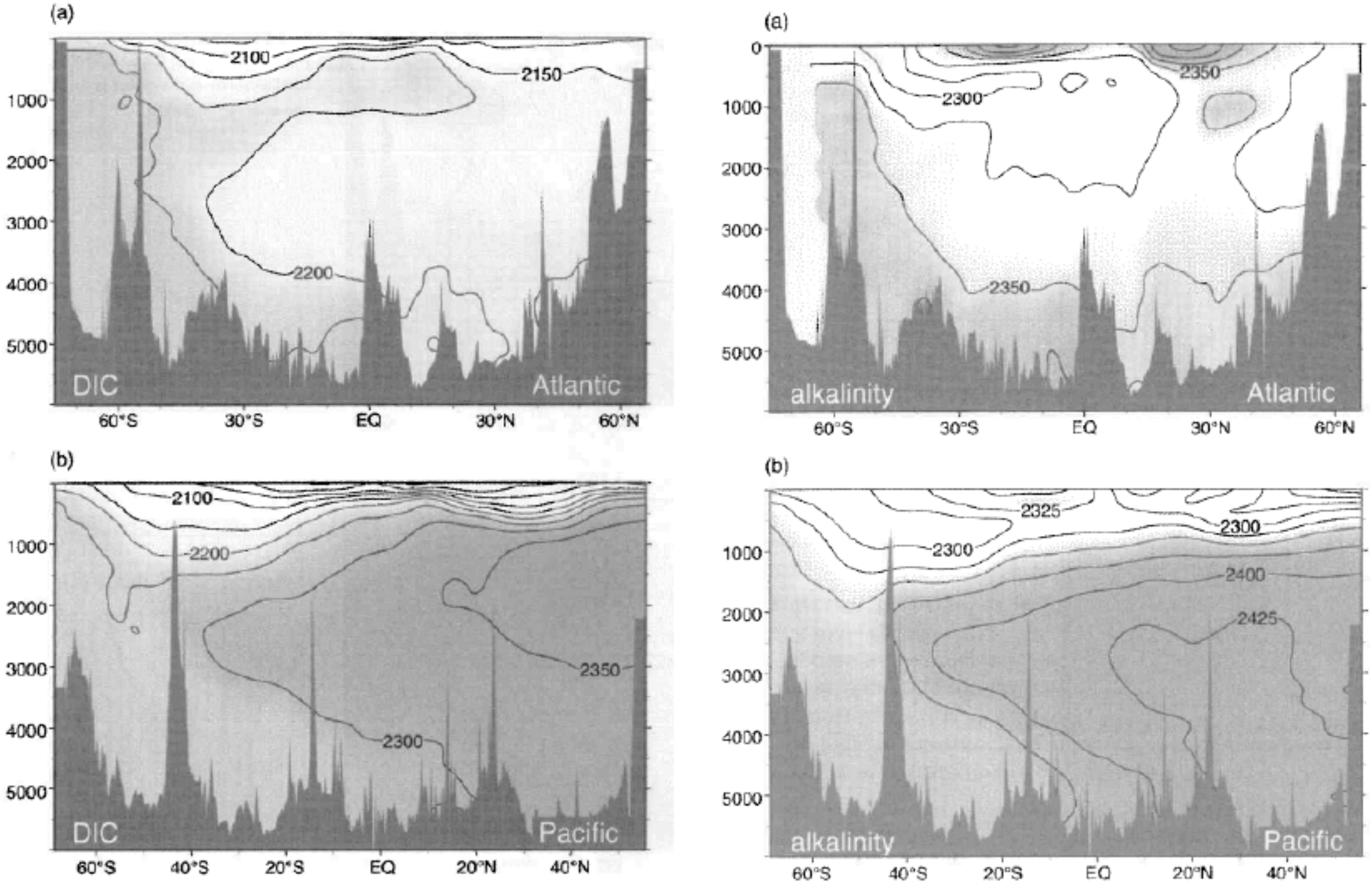
Arrows: Formation of OM reduces DIC (can increase Alk slightly): DOC ~ .1 DIC. Formation of CaCO$_3$ reduces DIC and Alk in a 1:2 ratio. The latter process is ~10x the former.

Dissolved Inorganic Carbon



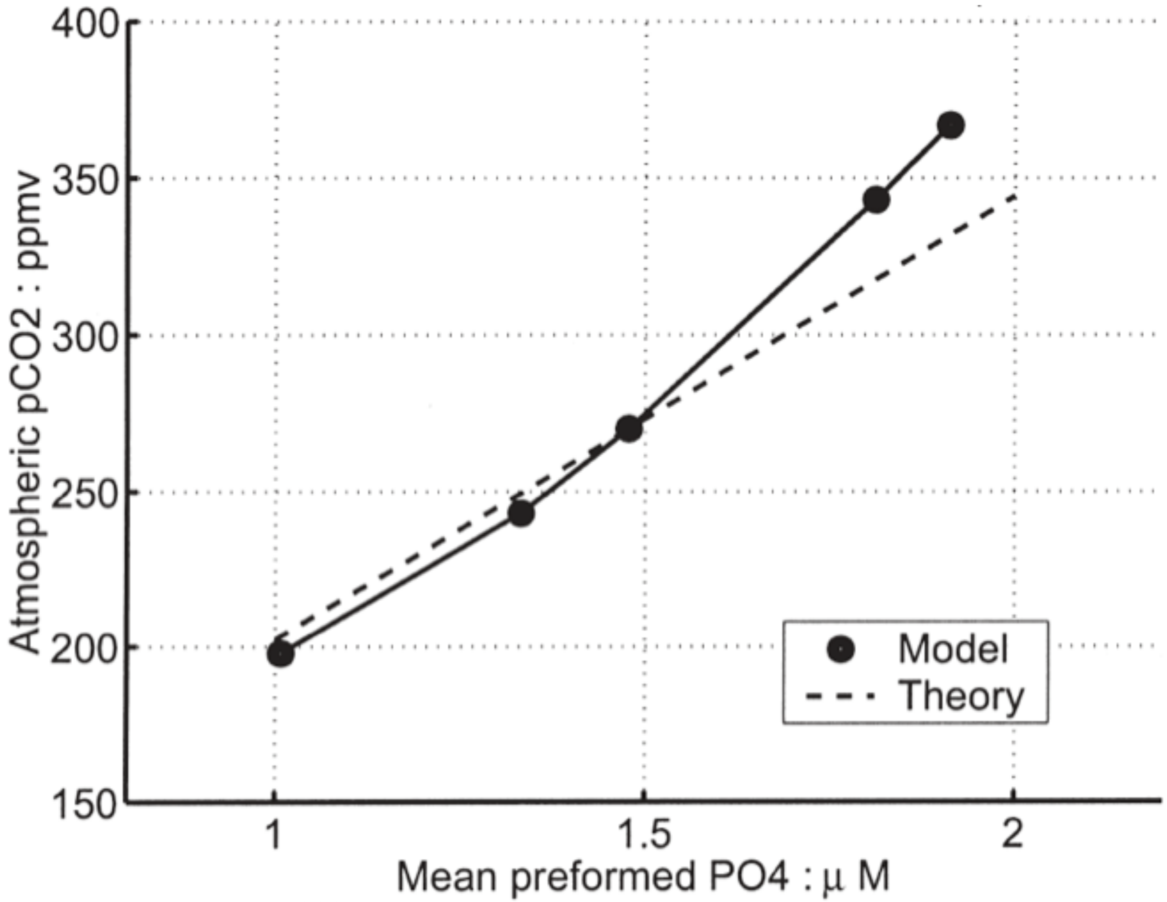
The distribution of DIC across depth and two ocean basins, caused primarily by the addition of DIC from respiration of OM, but also by solubility and $CaCO_3$ dissolution. E.g., low DIC in Atlantic because younger water with less respiration as yet. Notice the broad similarity with remineralized nutrients (e.g., slide 6).

DIC and Alkalinity in the Atlantic and Pacific



Analogous to the DIC pumps, the vertical pumps for Alkalinity are (a) P-E decreases Alk ($n.b.$, subtropical surface Atlantic), (b) NO_3 remineralization increases Alk, and (c) $CaCO_3$ dissolution increases ionization.

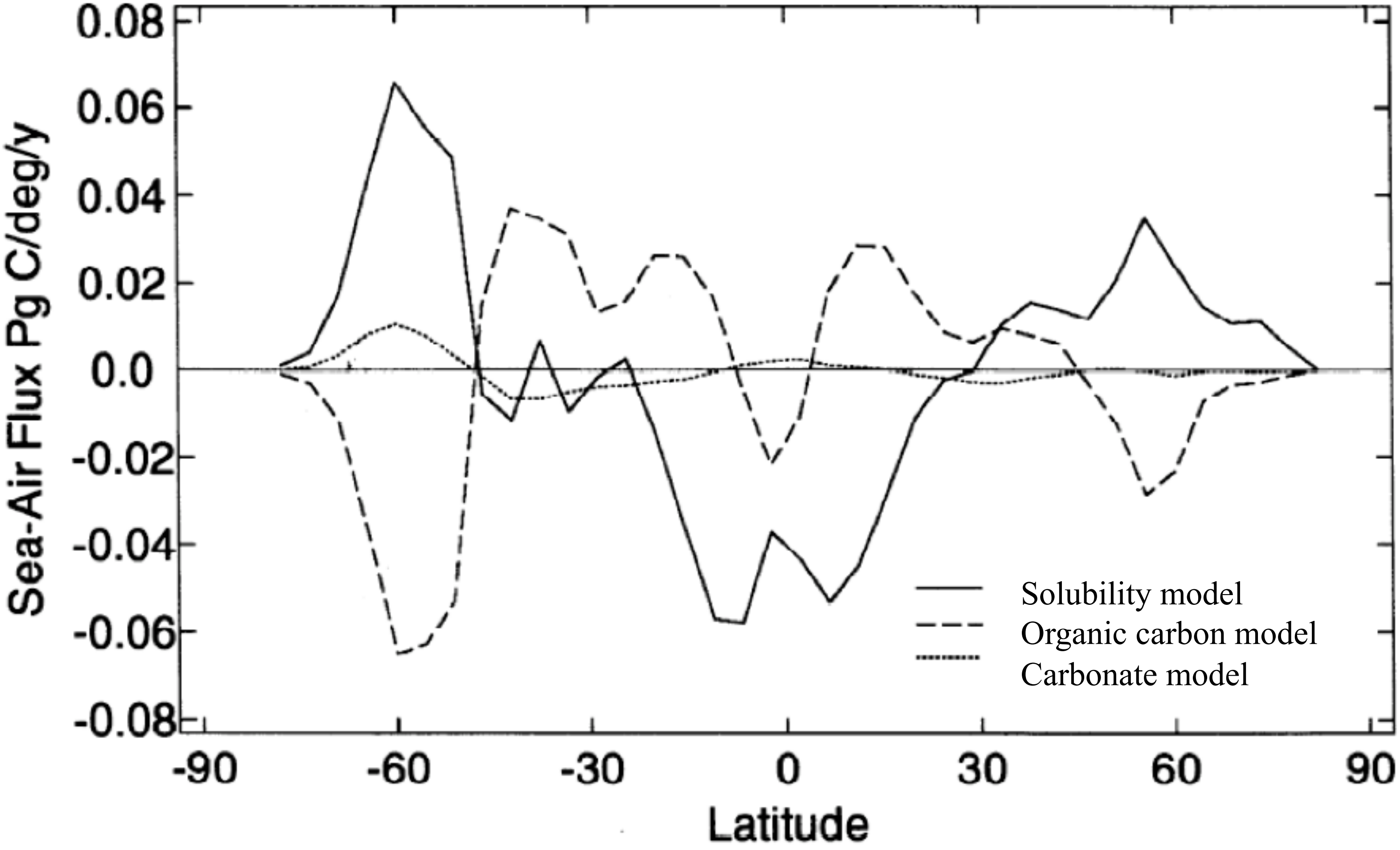
pCO_2 and organic pump



Ito et al. [2005]

A strong sensitivity of atmospheric CO_2 to "pre-formed" nutrients (i.e., conditions in the mixed layer) that do not get used by plankton before being transported into ocean interior, and therefore do not transport and DIC to depth. In ice ages, more dust (Fe) and slower MOC lead to greater subpolar consumption, less surface PO_4, less pCO_2. The ocean has a large, variable C reservoir by DIC partitioning and the 3 carbon pumps.

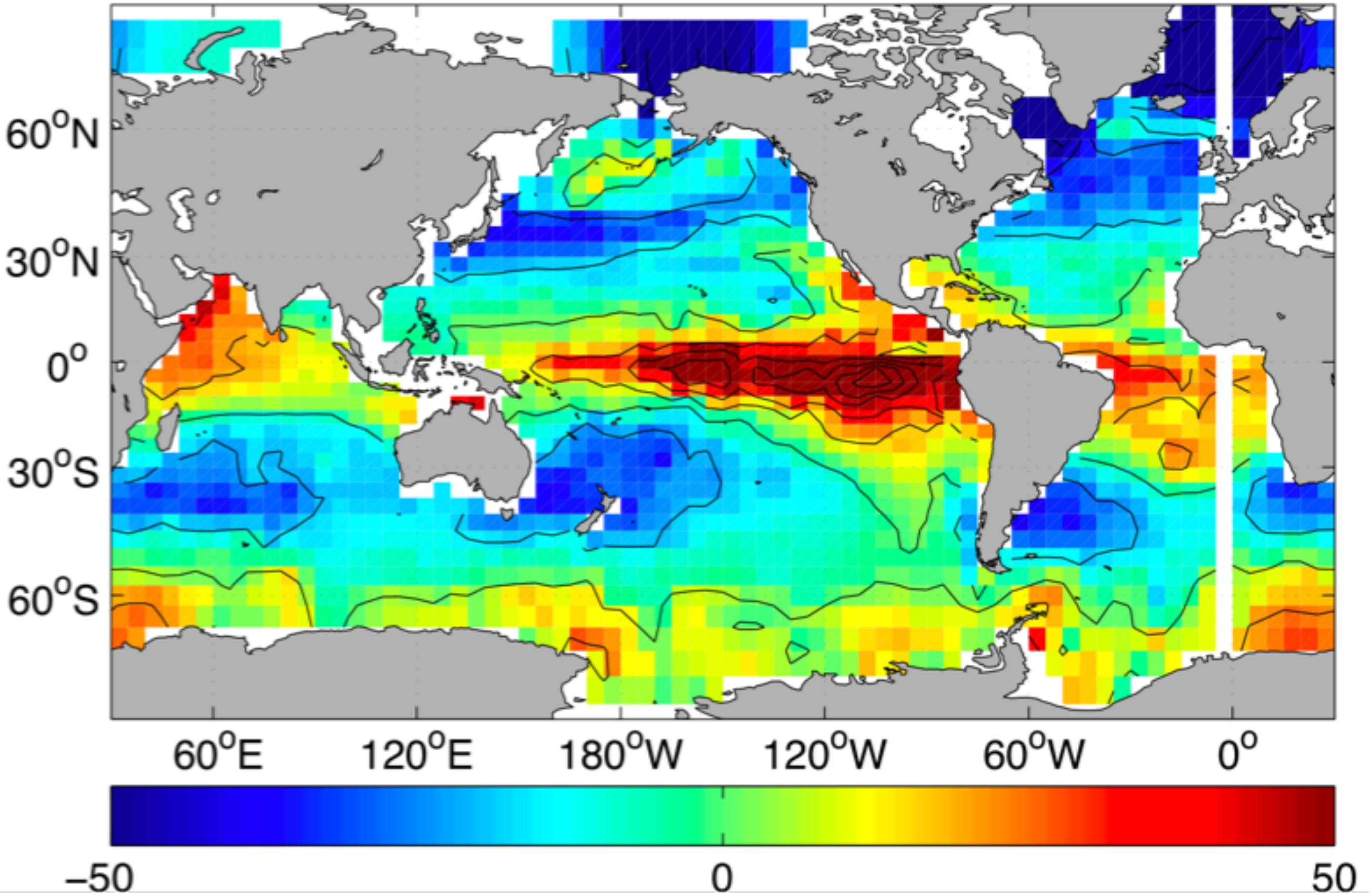
Air-Sea CO_2 fluxes



Preindustrial air->sea CO_2 fluxes from model simulations [Murnane et al. 1999]. The flux of CO_2 from ocean to atmosphere due to differences in partial pressure (ΔpCO_2) due to solubility pump (heating/cooling) and biological pump (mostly photosynthesis/respiration), are generally of opposite sign at high latitudes, relationship is more complex in low latitudes. Carbonate pump is a secondary effect.

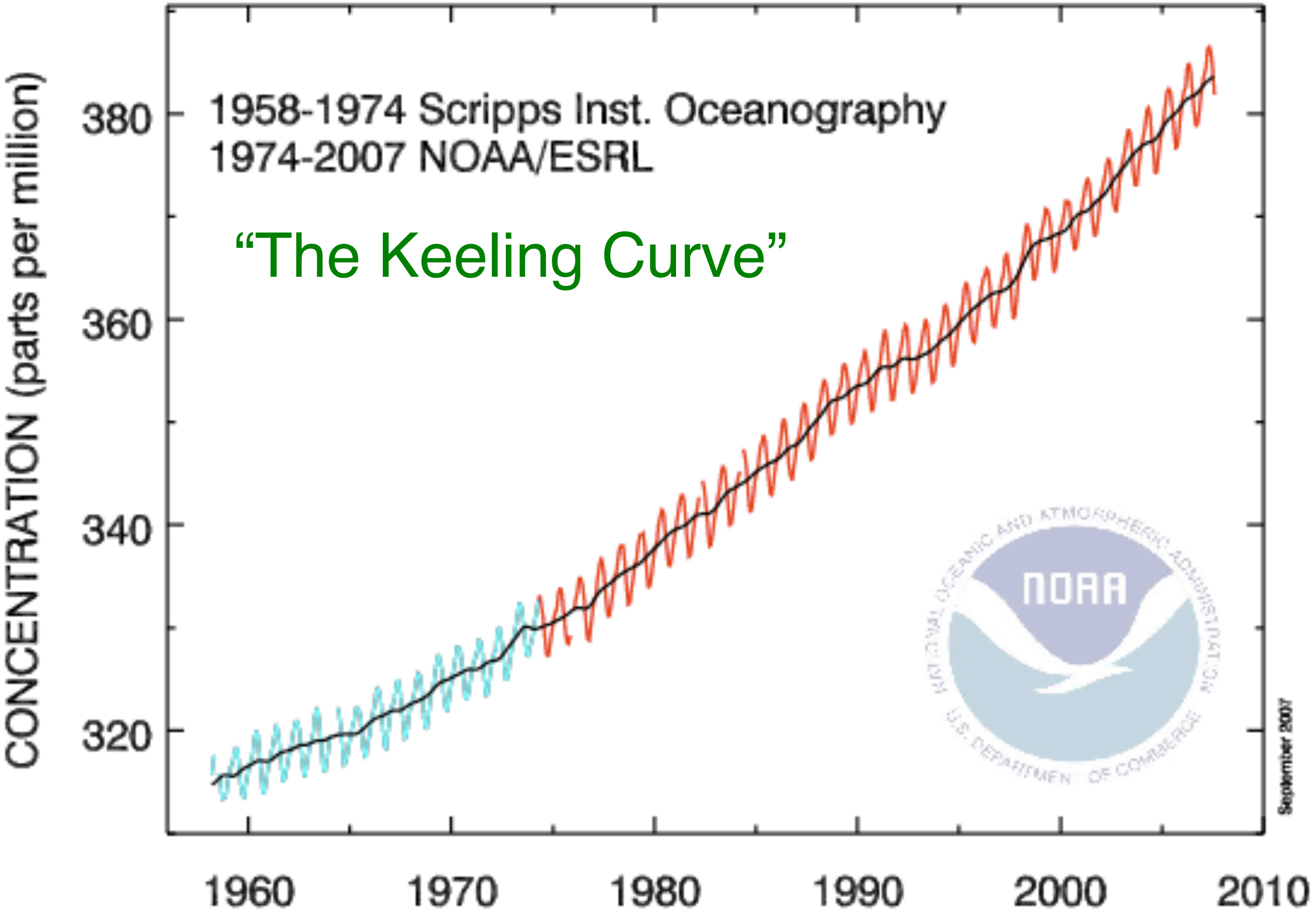
The biological pump includes both CO2 consumption and burial by organic processes and surfacing of DIC-rich interior water
The net air-sea flux is a generally small residual of the component fluxes (next slide).

Air-sea pCO_2 difference



Annual mean pCO2 difference ($pCO_2^{ocean} – pCO_2^{atmosphere}$; μatm) . The pCO2 differences induces an air-sea flux F_{CO2} (Henry's law). Variations are due almost entirely to ocean processes: heating (+), cooling (-), photosynthesis (-), and upwelling of respired DIC (+). Because of buffering, the equilibration time for CO_2 is ~20x slower than for other gases, ~ 1 year. High values in eastern tropical Pacific reflect heating (reduced solubility) and upwelled DIC, countering photosynthesis and leading to CO_2 flux into the atmosphere. Low polar values due to cooling and productivity.

Anthropogenic CO_2



“The Keeling Curve”

m

As of the mid-1990’s, fossil fuel burning had released about 245 GtC into the atmosphere (currently ~6.5 GtC/yr and accelerating). The amount remaining in the atmosphere is only ~165 GtC. Where’s the other ~80 GtC? Answer: about 120 GtC into the ocean and about -30 GtC from the land surface (deforestation).

Ocean CO_2 uptake

In the 1990's CO_2 was measured throughout the ocean. How much was due to "anthropogenic" sources?

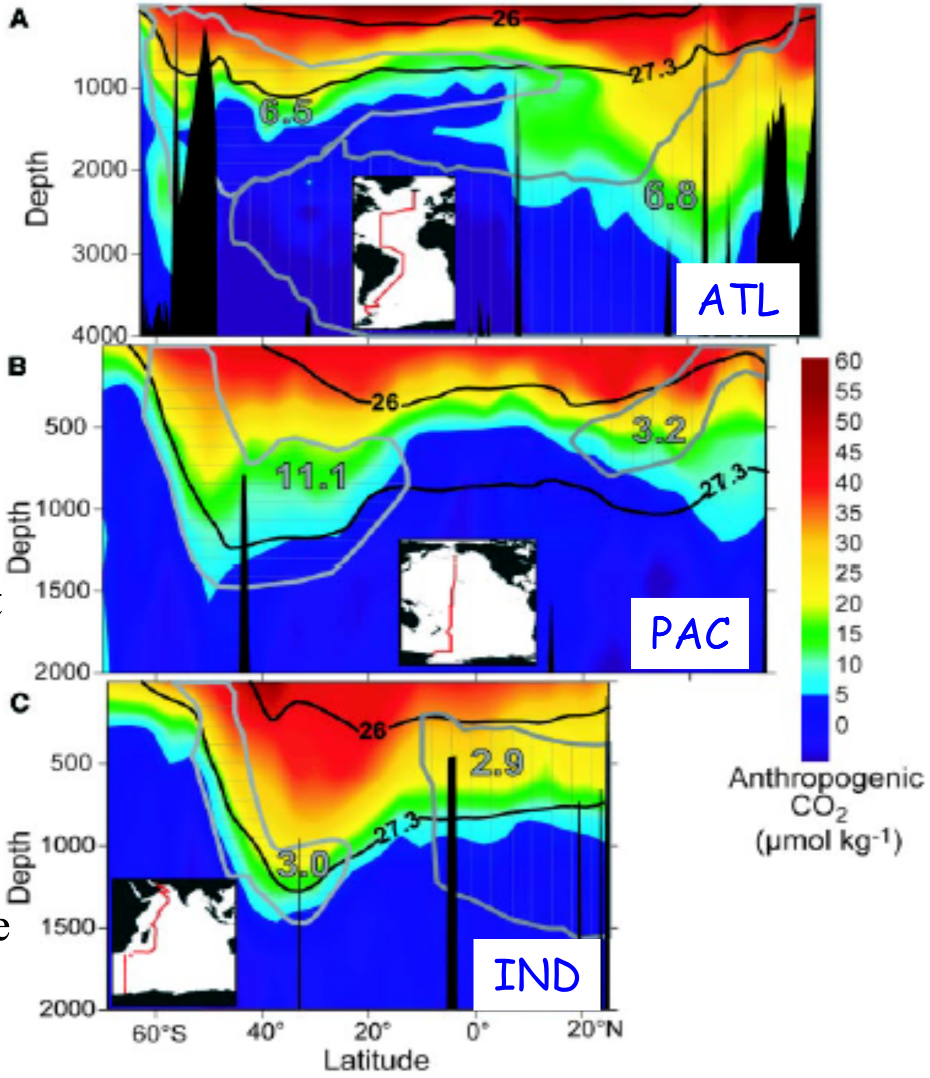
$$C_{obs} = C_{eq}^{280} + C_{diseq} + C_{bio} + C_{anthr}$$

By measuring T and S, we can estimate the equilibrium CO_2 concentration under a preindustrial atmosphere (280 ppm).

A preformed disequilibrium is estimated by tracing water mass origins to the surface (assuming constant C_{diseq}).

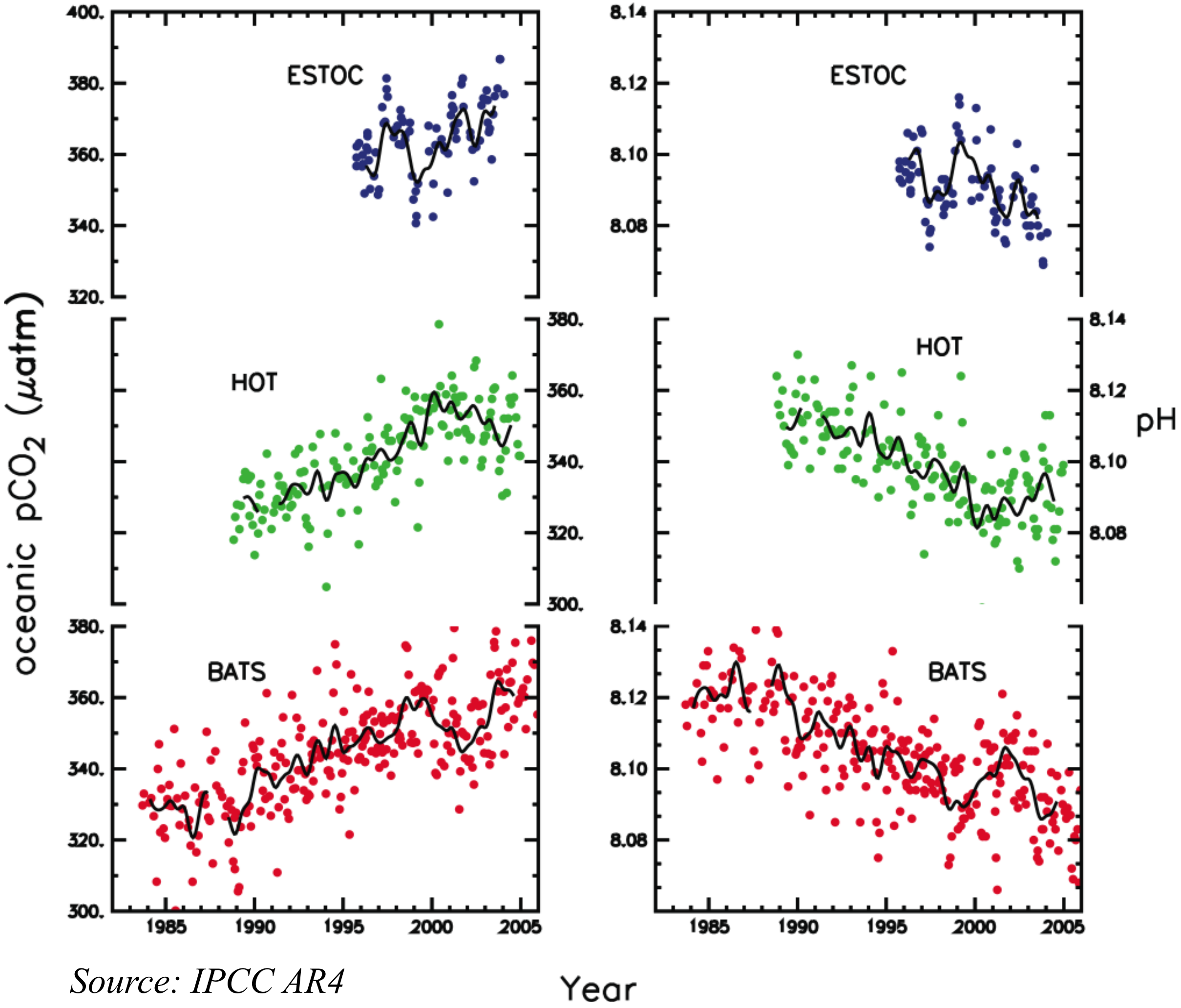
By measuring AOU and Alk, we can estimate how much CO_2 present is due to biology (OM + $CaCO_3$).

The difference is anthropogenic CO_2 absorbed by the ocean due to rising atmospheric CO_2: the warm water sphere has more because of Ekman MOC (80 Sv) > THC MOC (20 Sv) and because DIC is larger at high latitude. Saturation is approaching as Alk decreases, carbonate decreases, and CO_2 increases.



Total ~120 GtC

Ocean acidification

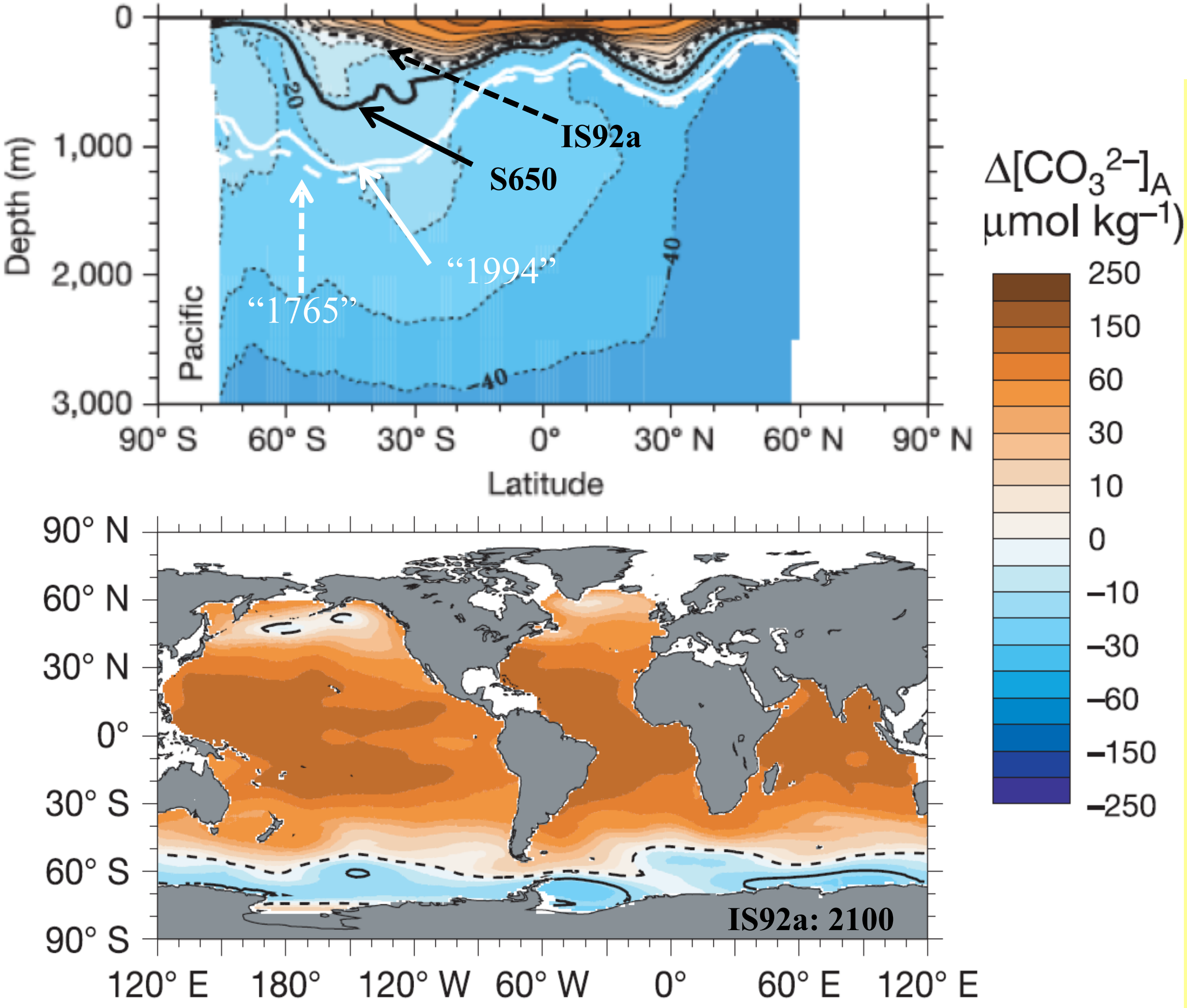


Source: IPCC AR4

Measured surface pCO_2 (left) and pH (right) at time-series sites at Eastern North Atlantic (Canary I.), Central North Pacific (Hawaii), Western North Atlantic (Bermuda).

The most obvious direct consequence of increasing CO_2 is the reduction of pH and Alk. This leads toward undersaturation of CO_3, hence dissolution of shells and increase of CO_2 partition fraction.

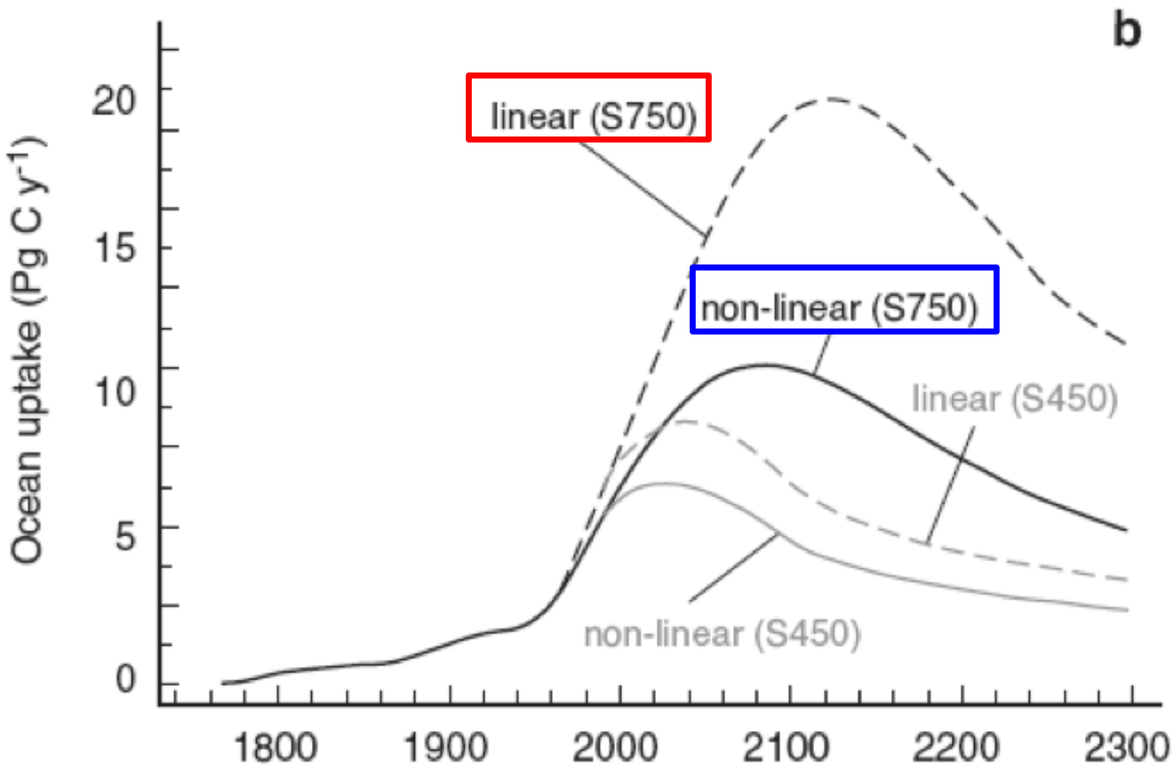
$CaCO_3$ Undersaturation



Orr et al. [2005]

Predicted undersaturation of CO_3 with respect to the pressure-dependent solubility of $CaCO_3$ shells. (Solubility of $CaCO_3$ increases with pressure.) Marginal saturation lines are drawn on upper plot for past years and indicated global warming scenarios (S650, IS92a); contours are for IS92a. The reduction of [CO_3^{2-}] due to ocean acidification will first lead to undersaturation in places where waters are already high in DIC (i.e. upwelling zones). Calcification stops when waters become undersaturated, and may slow down well before that.

Declining CO_2 Uptake Capacity



“linear” = no change in ocean pH, $[CO_3^{2-}]$

“non-linear” = decreasing ocean pH, $[CO_3^{2-}]$

Sarmiento and Gruber [2006]

Projected oceanic uptake of anthropogenic CO_2 from a simple ocean model forced by emissions scenarios that stabilize atmospheric CO_2 at 450 ppm (S450) and 750 ppm (S750). The acidification of seawater (in “non-linear” models) reduces the buffering capacity to further absorb CO_2 from the atmosphere with reduced pH, relative to a non-reactive dye tracer (“linear” models). This is a positive feedback on atmospheric greenhouse concentrations with continuing emissions.