Ocean biogeochemistry

CESM Tutorial

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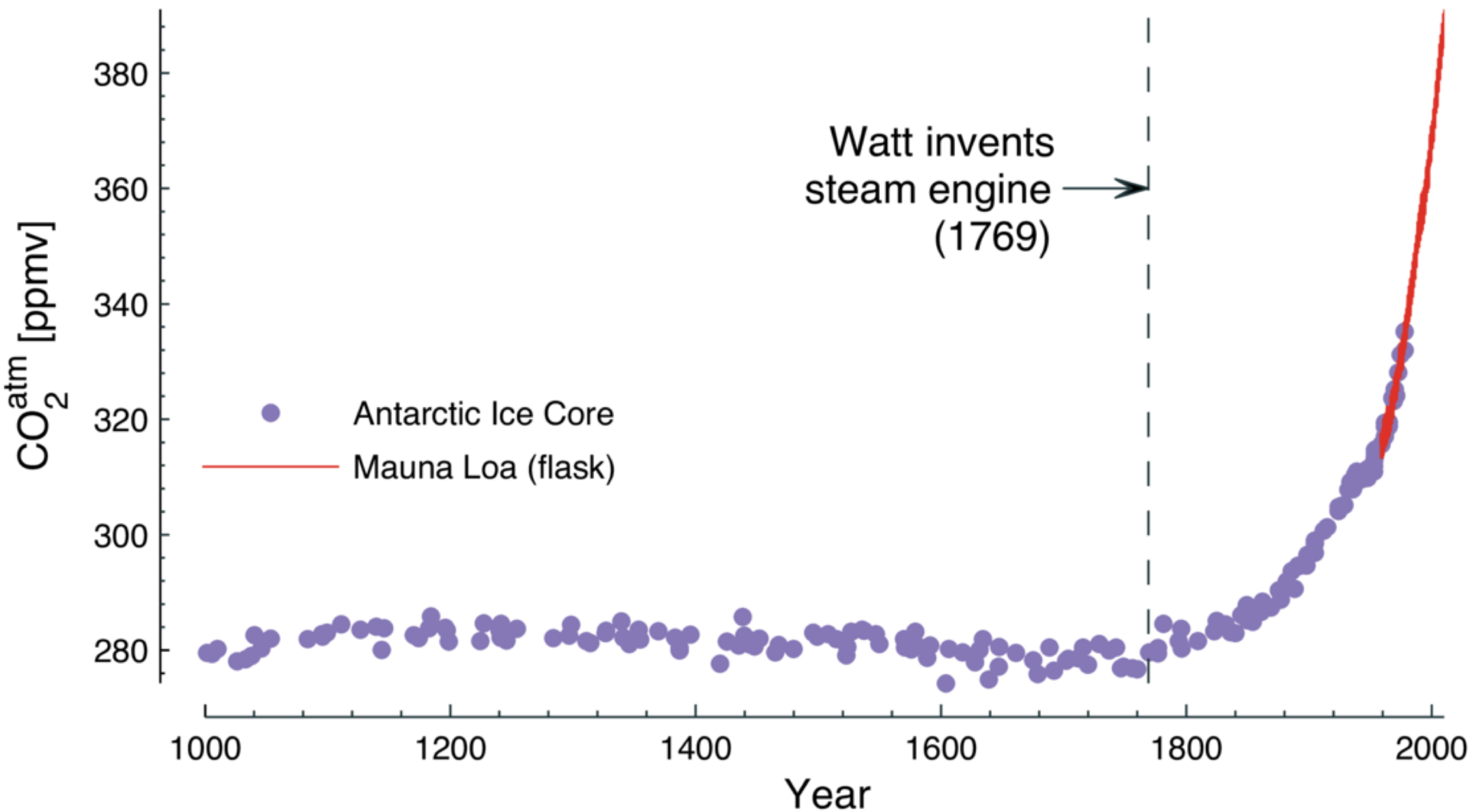
August 2018

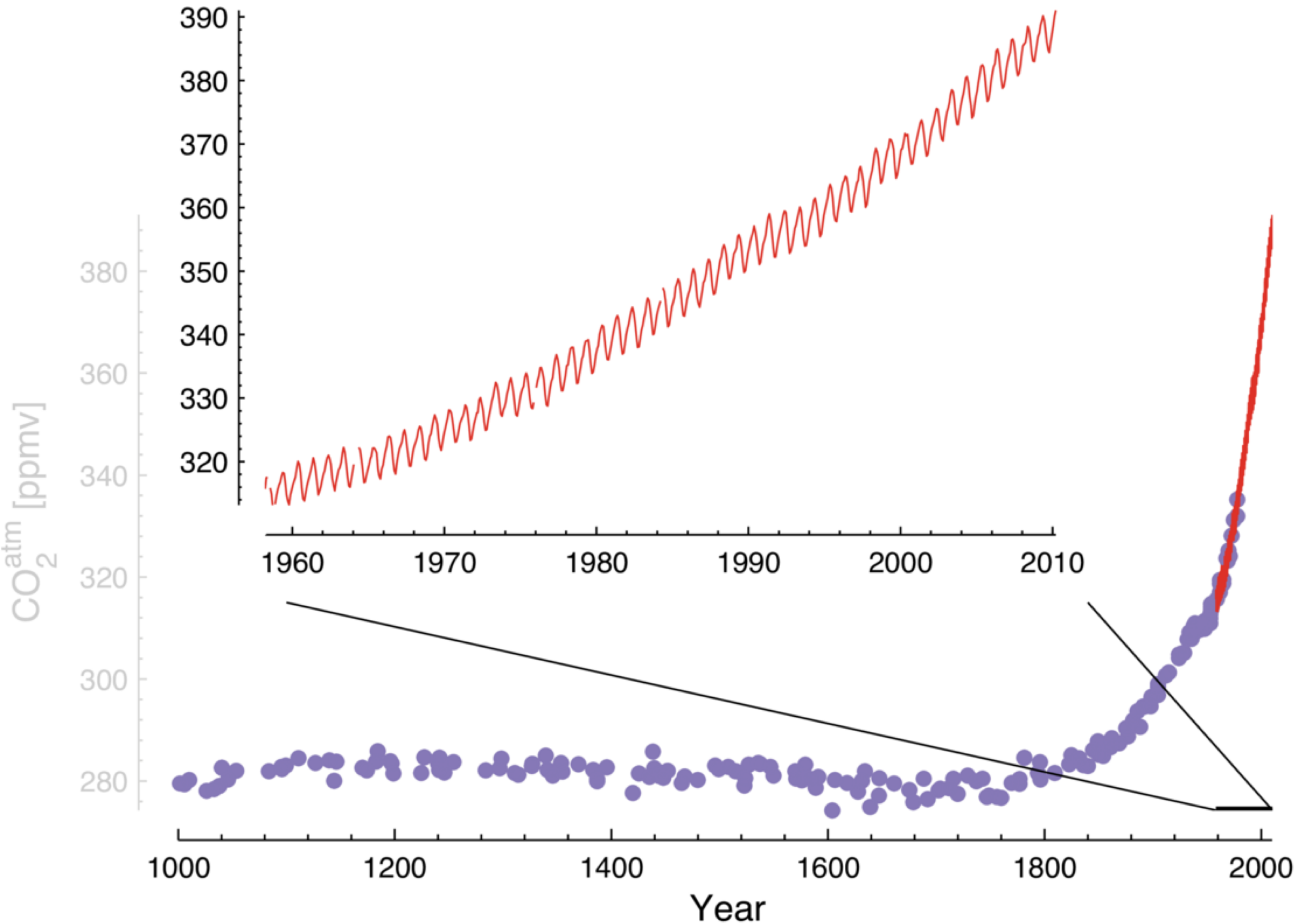
NATIONAL CENTER FOR ATMOSPHERIC RESEARCH

Atmospheric CO_2



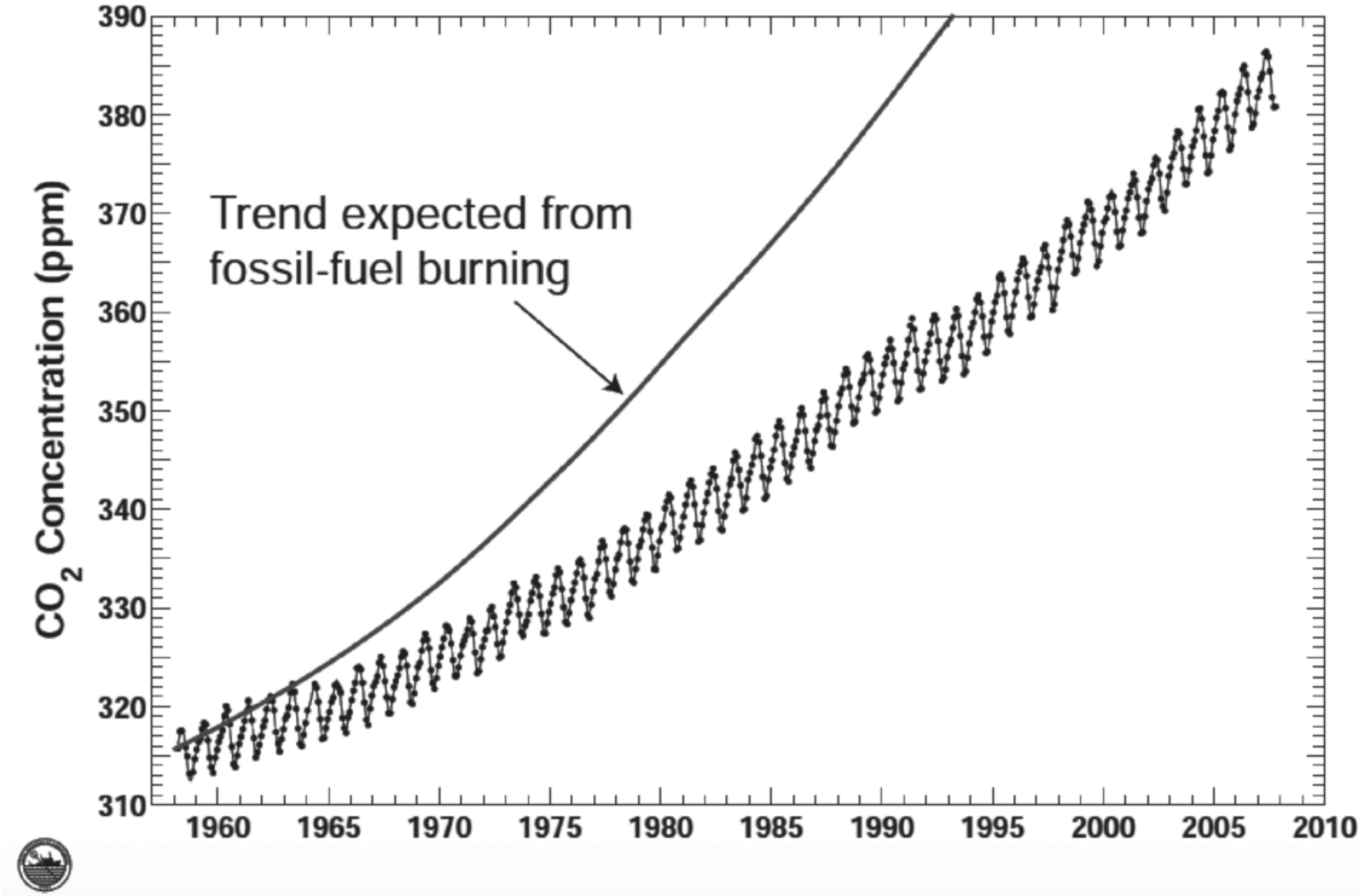
Global carbon cycle

Atmospheric CO_2



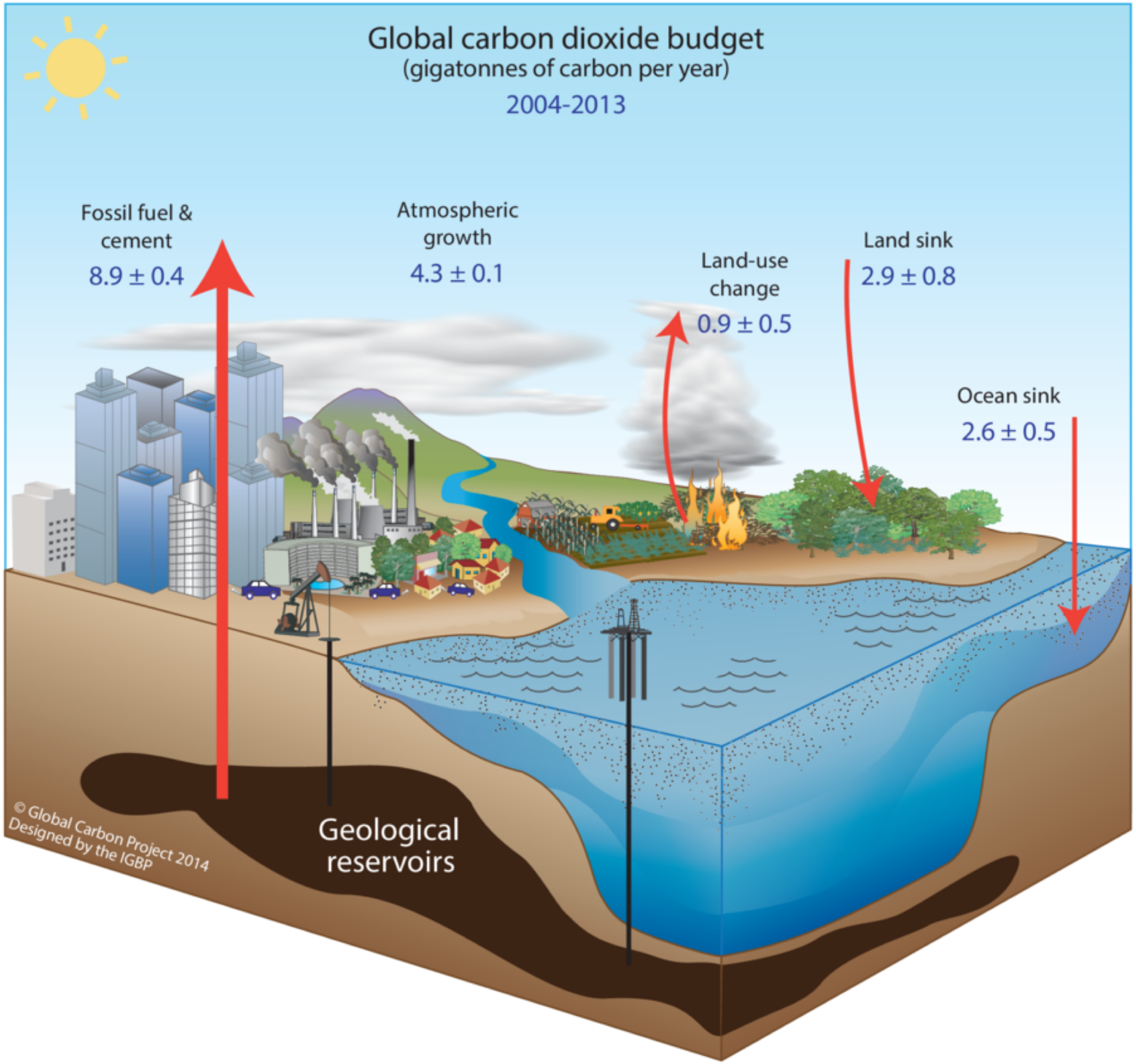
CO_2 accumulation in the atmosphere mitigated by natural sinks

Mauna Loa CO_2 Record



R. Keeling

Fate of anthropogenic CO_2



Outline

Ingredients for an ocean biogeochemistry model

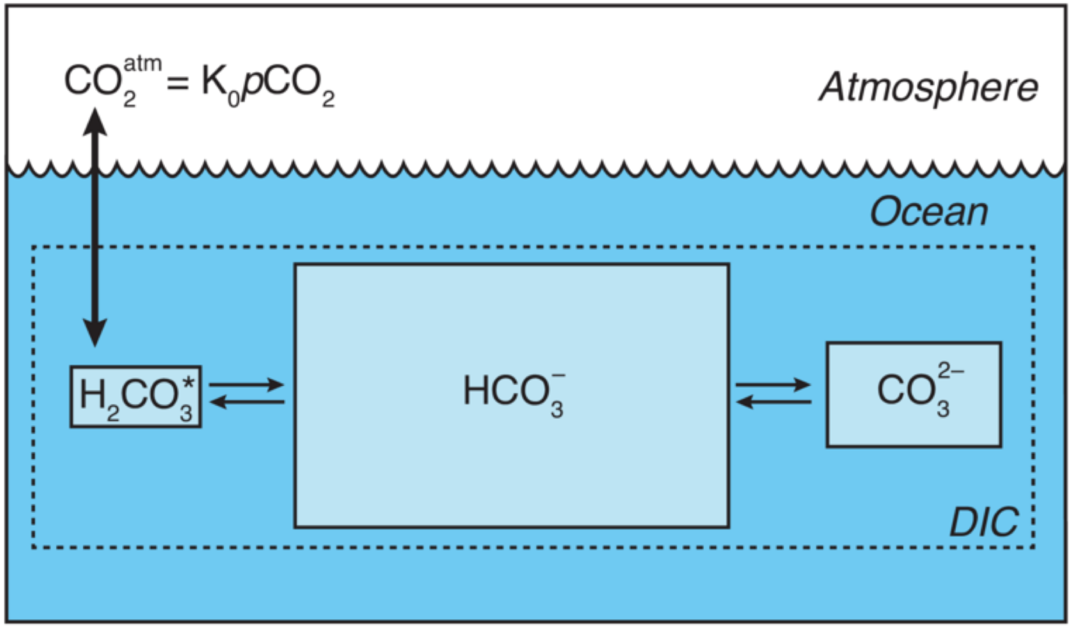
1. Inorganic carbonate chemistry
    - Total CO_2 in seawater depends on acid-base equilibria
2. Marine ecosystem dynamics (the 'biological pump')
    - Carbon and nutrient cycles are coupled via organic matter production
    - Sinking organic matter transfers carbon to the deep ocean

Applications and validation

3. Flow-dependent biases in transient tracer uptake and mean state
4. Coupled carbon-climate feedbacks
5. Atmospheric CO_2 distributions

Dissolved inorganic carbon

$$DIC = \underset{\sim 0.5\%}{[H_2CO_3^*]} + \underset{\sim 88.6\%}{[HCO_3^-]} + \underset{\sim 10.9\%}{[CO_3^{2-}]}$$



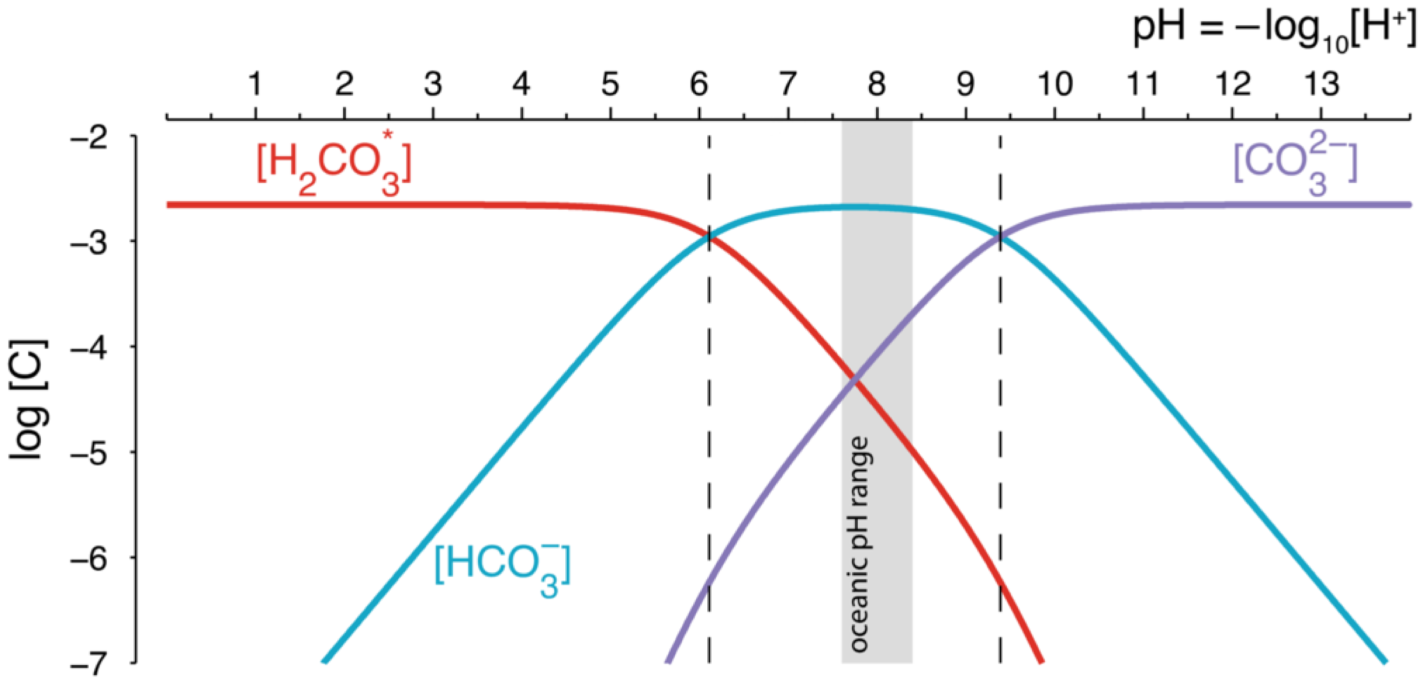
$$CO_{2,g} + H_2O \rightleftharpoons H_2CO_3^*$$
$$H_2CO_3^* \rightleftharpoons H^+ + HCO_3^-$$
$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

$$H_2CO_3^* = CO_{2,aq} + H_2CO_3$$

Equilibrium relationships (empirically determined)

$$K_0 = \frac{[H_2CO_3^*]}{pCO_2}, \; K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]}, \; K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

Carbonate speciation



Inorganic carbon chemistry: acid-base balance of seawater

Dissolved inorganic carbon (“total CO_2”)

$$DIC = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$$

Alkalinity (“buffer capacity”)

$$Alk = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] + [B(OH)_4^-] + \text{minor bases}$$

Additional reactions affecting pH

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$H_3BO_3 + H_2O \rightleftharpoons H^+ + B(OH)_4^-$$

$$K_w = [H^+][OH^-], \; K_B = \frac{[H^+][B(OH)_4^-]}{[H_3BO_3]}$$

Inorganic carbon chemistry: system of equations

Unknowns

$$pCO_2,\ [H_2CO_3^*],\ [HCO_3^-],\ [CO_3^{2-}],\ [H^+],\ [OH^-],\ [B(OH)_4^-],\ [H_3BO_3],\ Alk,\ DIC$$

Equations

Along with the definitions of *Alk* and *DIC*, we have

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

$$K_w = [H^+][OH^-],\ K_B = \frac{[H^+][B(OH)_4^-]}{[H_3BO_3]},$$

and total boron conservation, described by constant proportionality to salinity

$$B_T = [B(OH)_4^-] + [H_3BO_3] = c \cdot S$$

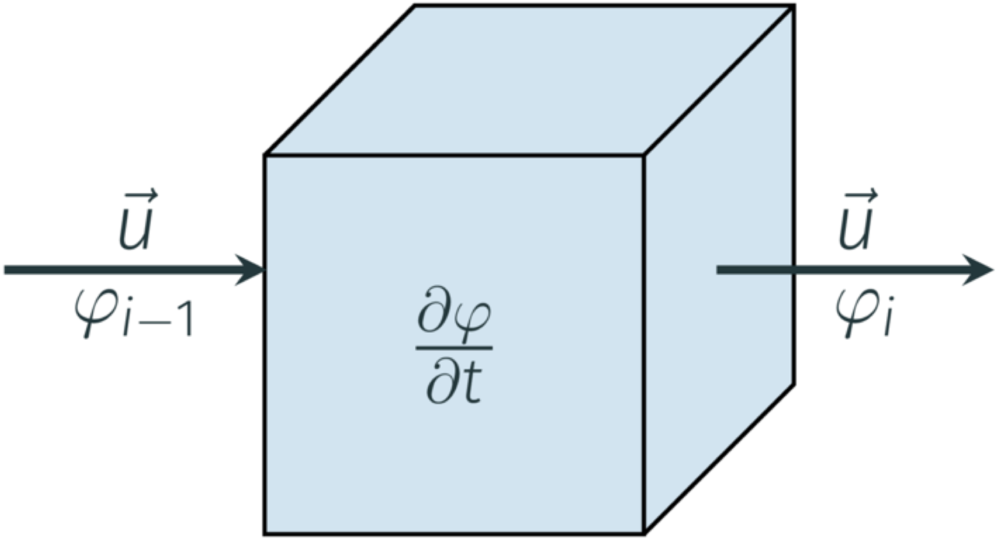
- 8 equations; 10 unknowns: need to specify 2 unknowns.

Modeling ocean carbon: prognostic tracers *DIC* and *Alk*

Prognostic variables ($\varphi = DIC,\ Alk$)

$$\frac{\partial \varphi}{\partial t} + \nabla \cdot (\vec{u}\varphi) - \nabla \cdot (K \nabla \varphi) = J(\varphi)$$

where $J(\varphi)$ = source/sink terms (biology!).



Modeling ocean carbon: prognostic tracers *DIC* and *Alk*

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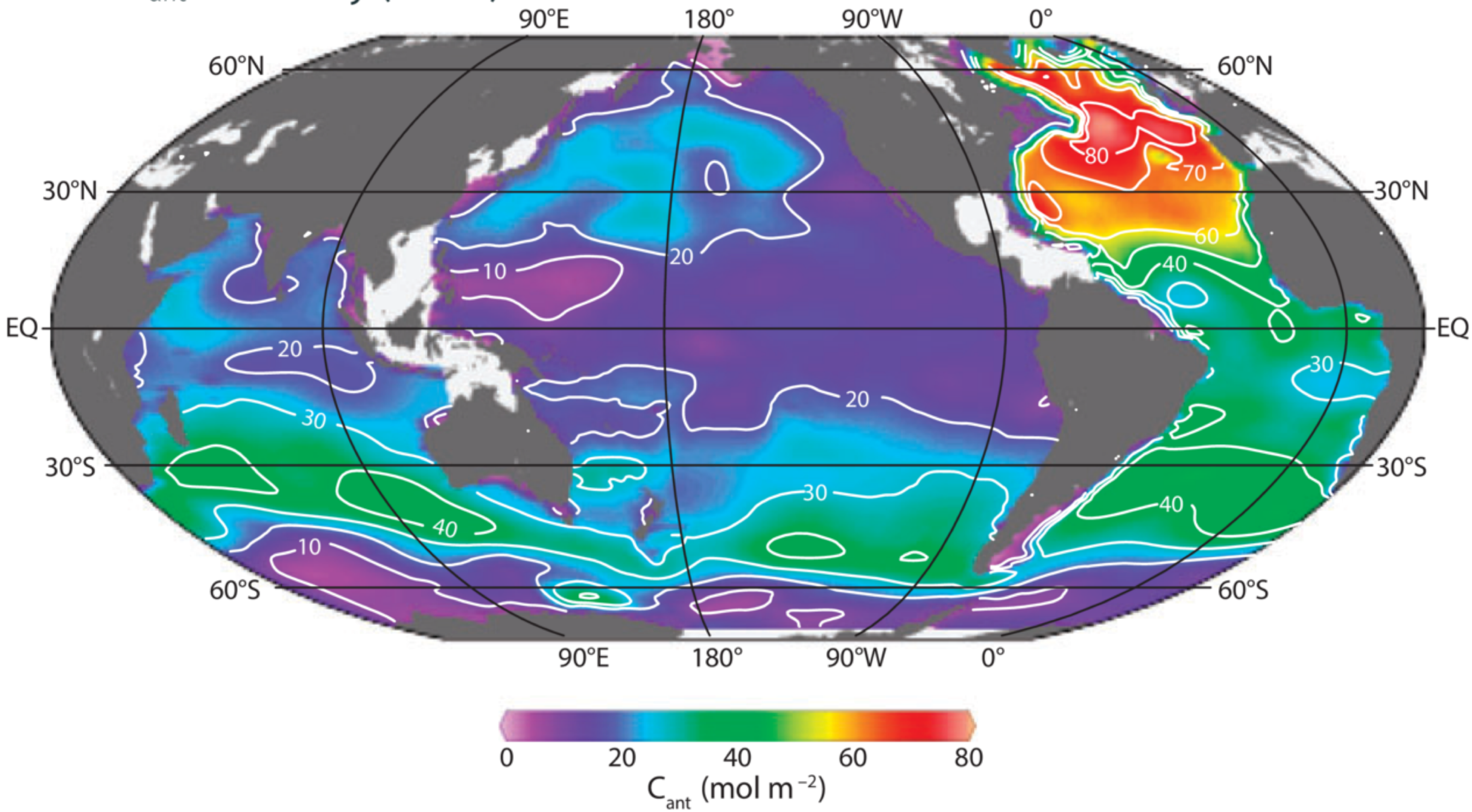
Diagnostic variables

1. Rearrange expression for *Alk*, solve for $[H^+]$ numerically (Newton-Raphson)
2. $[HCO_3^-] = \frac{(DIC)K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2}$, $[CO_3^{2-}] = \frac{(DIC)K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2}$
3. $[H_2CO_3^*] = \frac{[H^+][HCO_3^-]}{K_1}$
4. $pCO_2 = \frac{[H_2CO_3^*]}{K_0}$ → sea-to-air flux: $\boxed{F_{CO_2} = (1 - f_{ice})X_{kw}K_0(pCO_2^{ocn} - pCO_2^{atm})}$

Anthropogenic CO_2 uptake is mediated by circulation

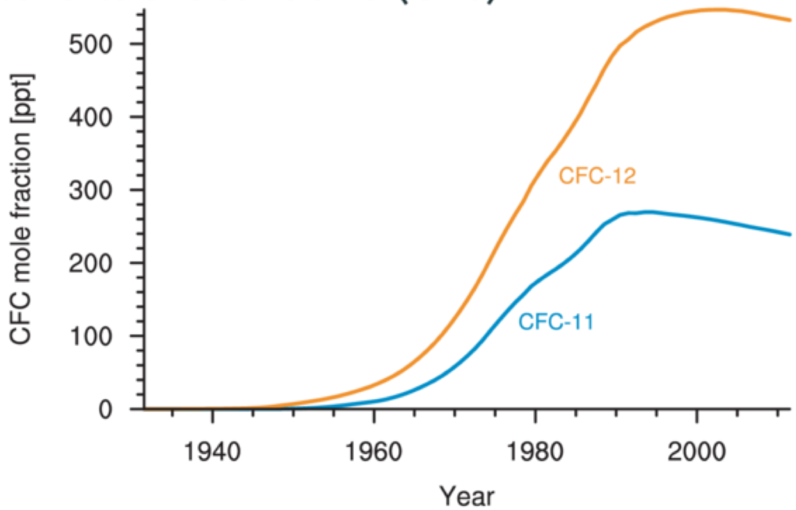
Ocean C_{ant} inventory (1990s)



Sabine et al. (2004) via Sabine & Tanhua (2010)

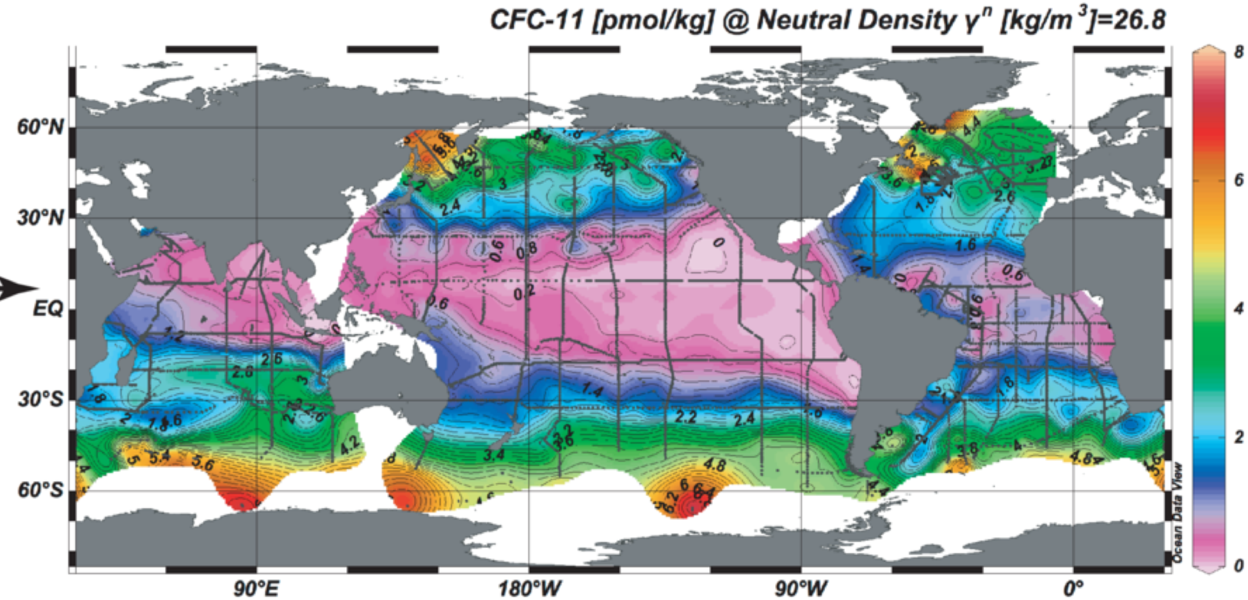
Observational constraints on ventilation processes

Chlorofluorocarbons (CFC)

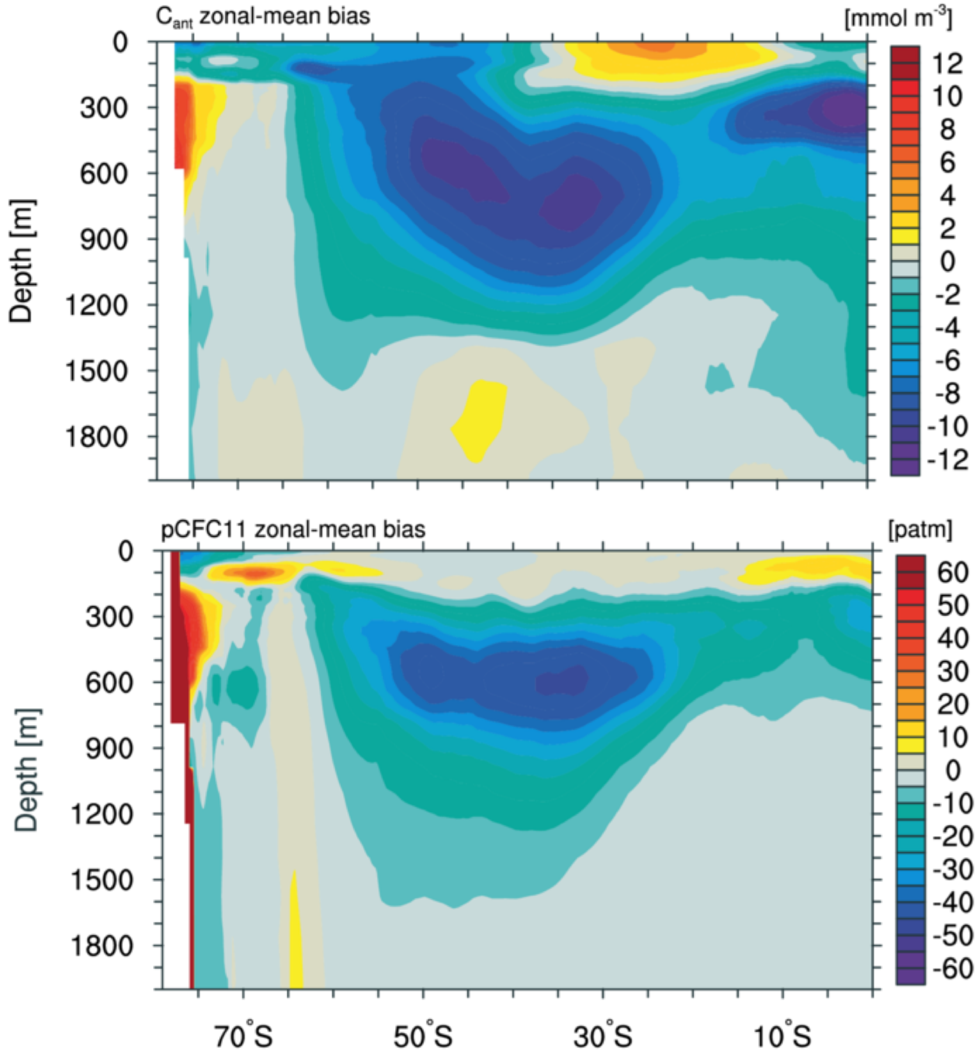


← Atmospheric history

Ocean observations →



CESM1: C_{ant} and pCFC biases



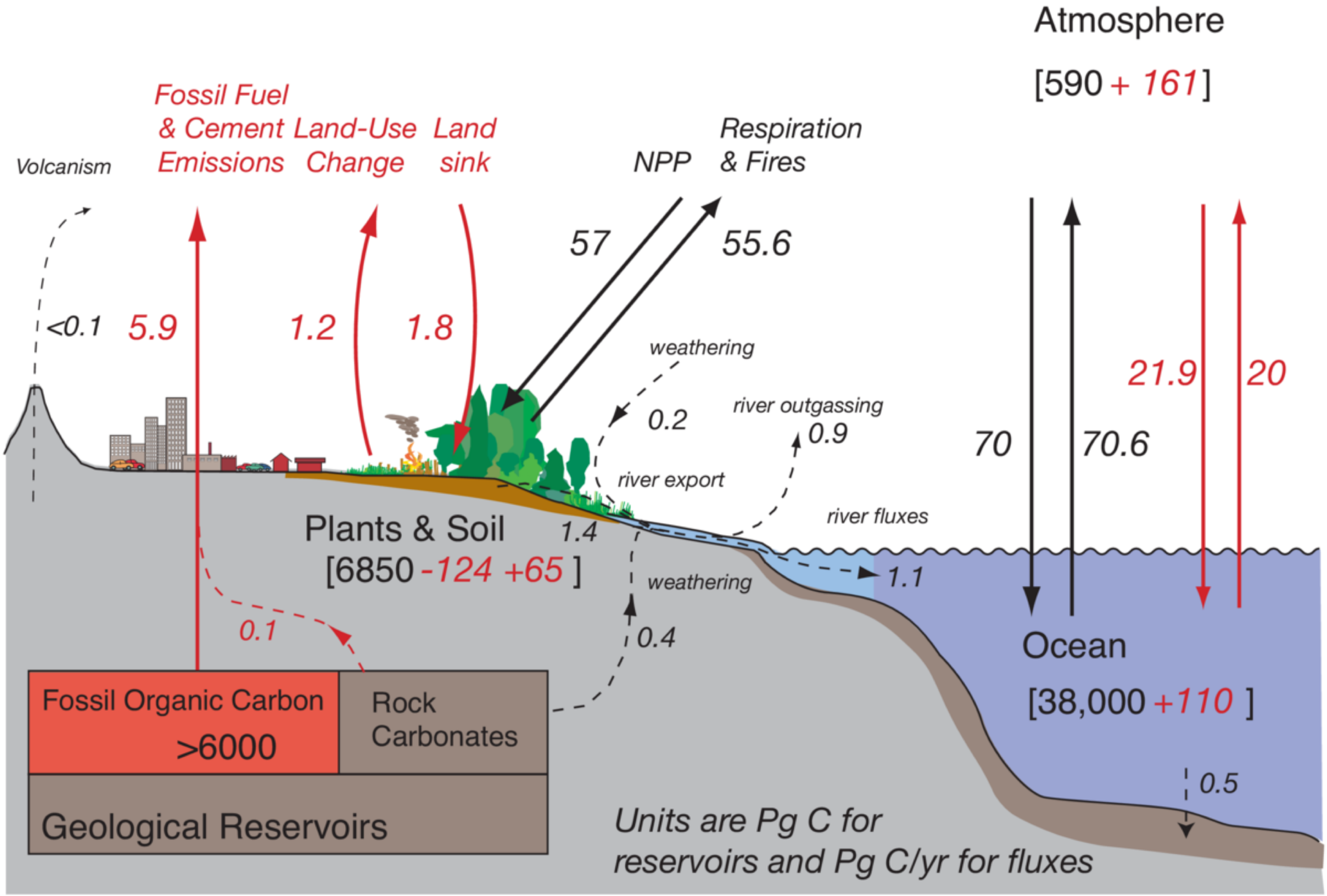
after Long et al., 2013

Hypotheses

- Mesoscale flow features;
- Vertical mixing;
- Missing physics: waves (i.e., Langmuir turbulence)?

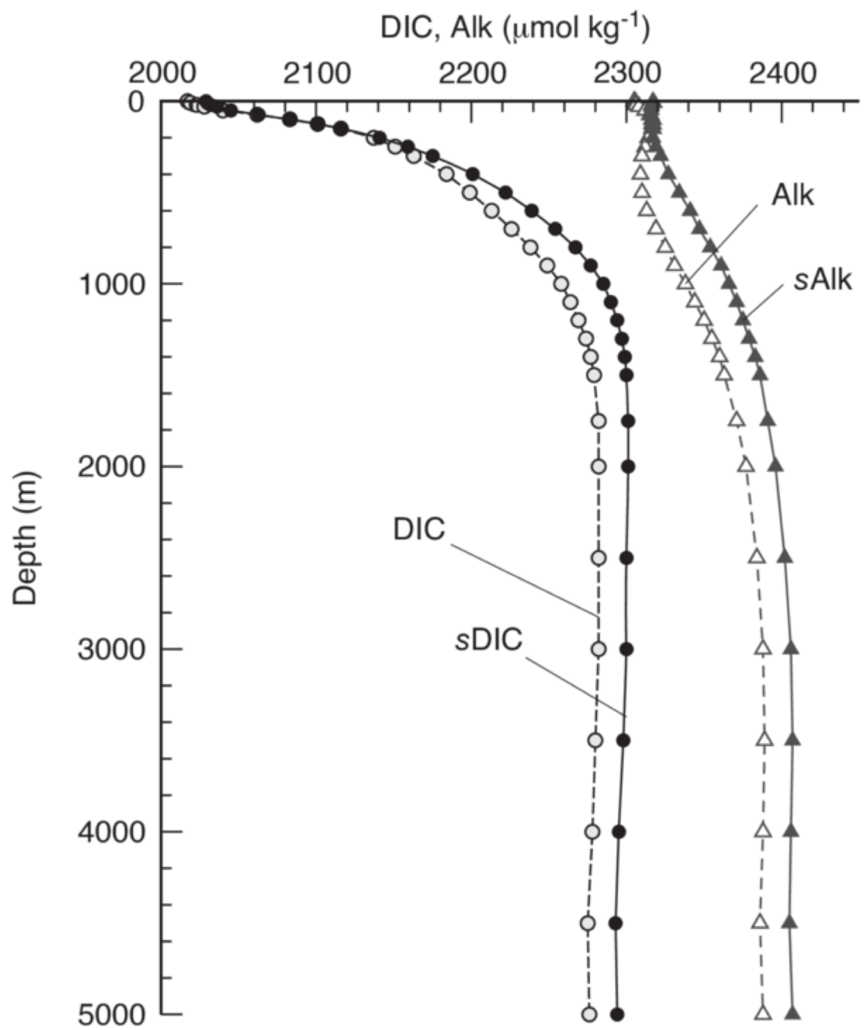
The ocean contains a vast natural C reservoir

The global carbon budget (c. 1990s)



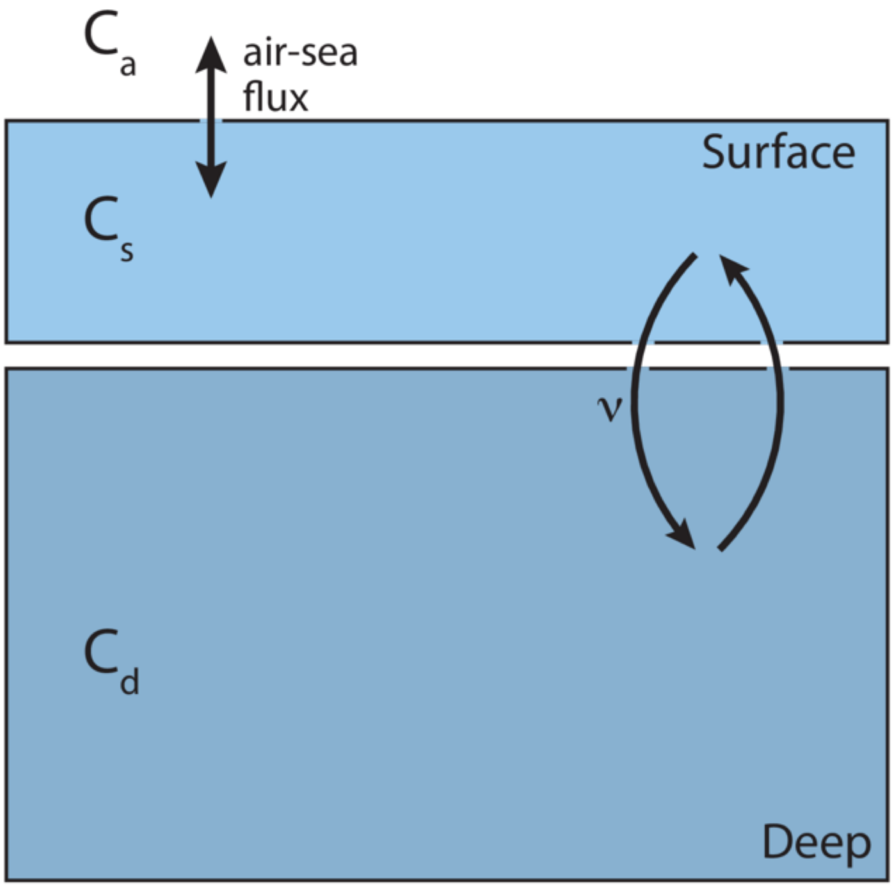
Variation of DIC with depth

Observed global-mean profile



Sarmiento & Gruber, 2006

Circulation homogenizes the ocean



Mass balance (deep box)

$$V_d \frac{dC_d}{dt} = \nu \left(C_s - C_d\right)$$

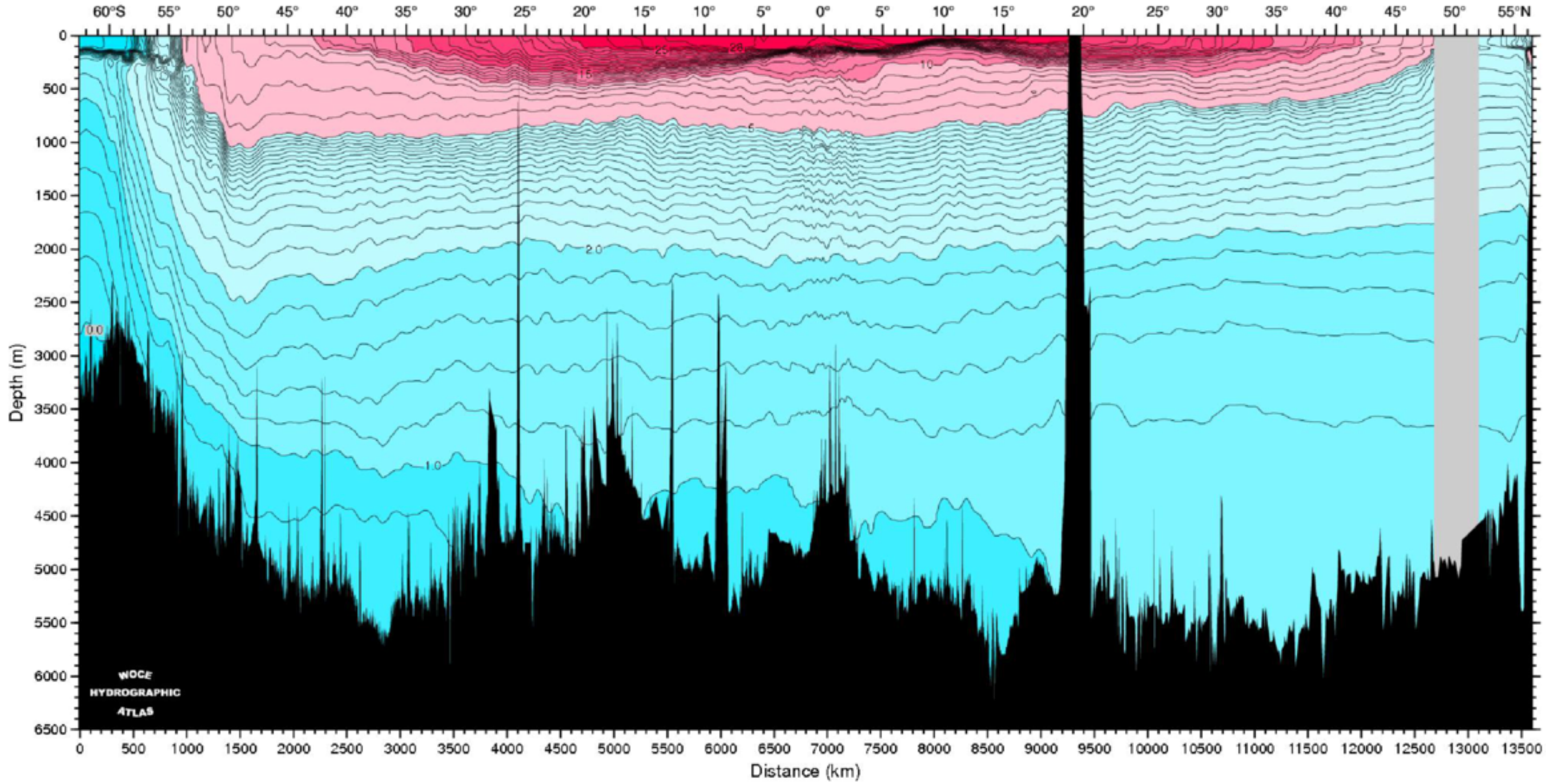
where

$$\begin{aligned} V_d &= \text{Volume of the deep box,} \\ \nu &= \text{Volume exchange rate,} \\ C_{s,d} &= \text{Concentrations in surface } (s) \\ &\quad \text{and deep } (d) \text{ boxes.} \end{aligned}$$

Steady-state

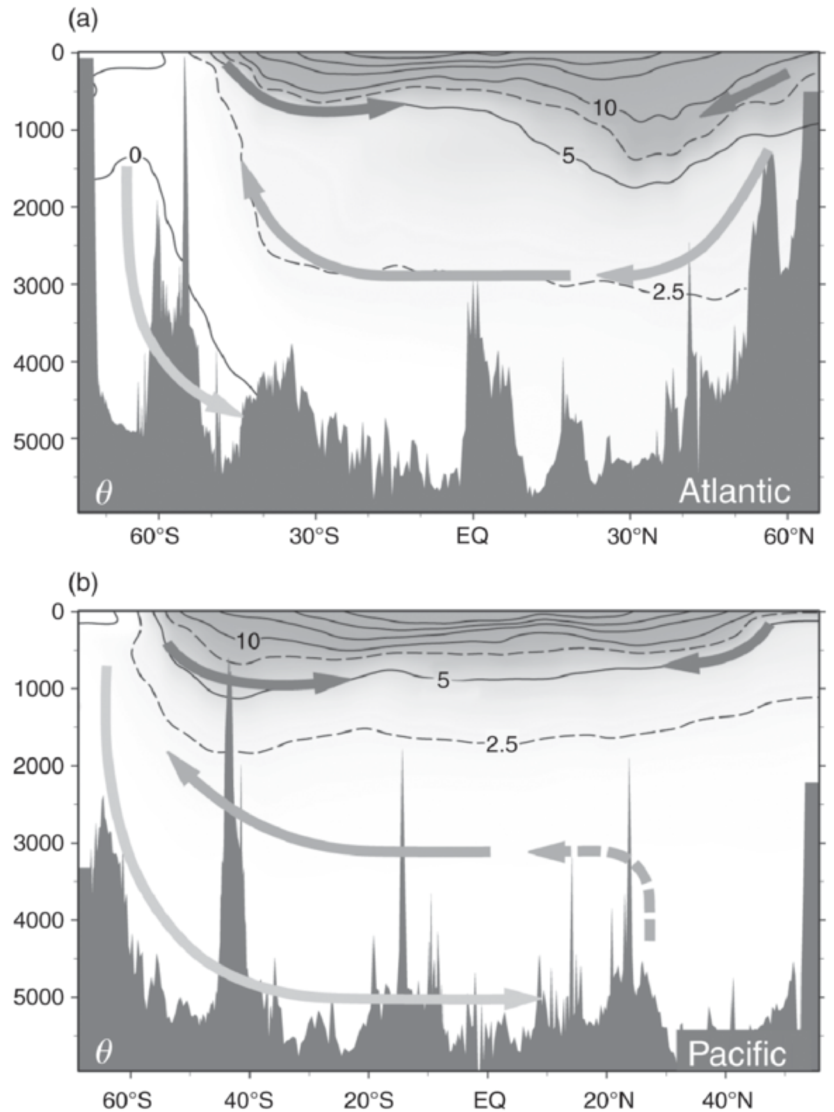
$$C_d = C_s$$

Potential temperature

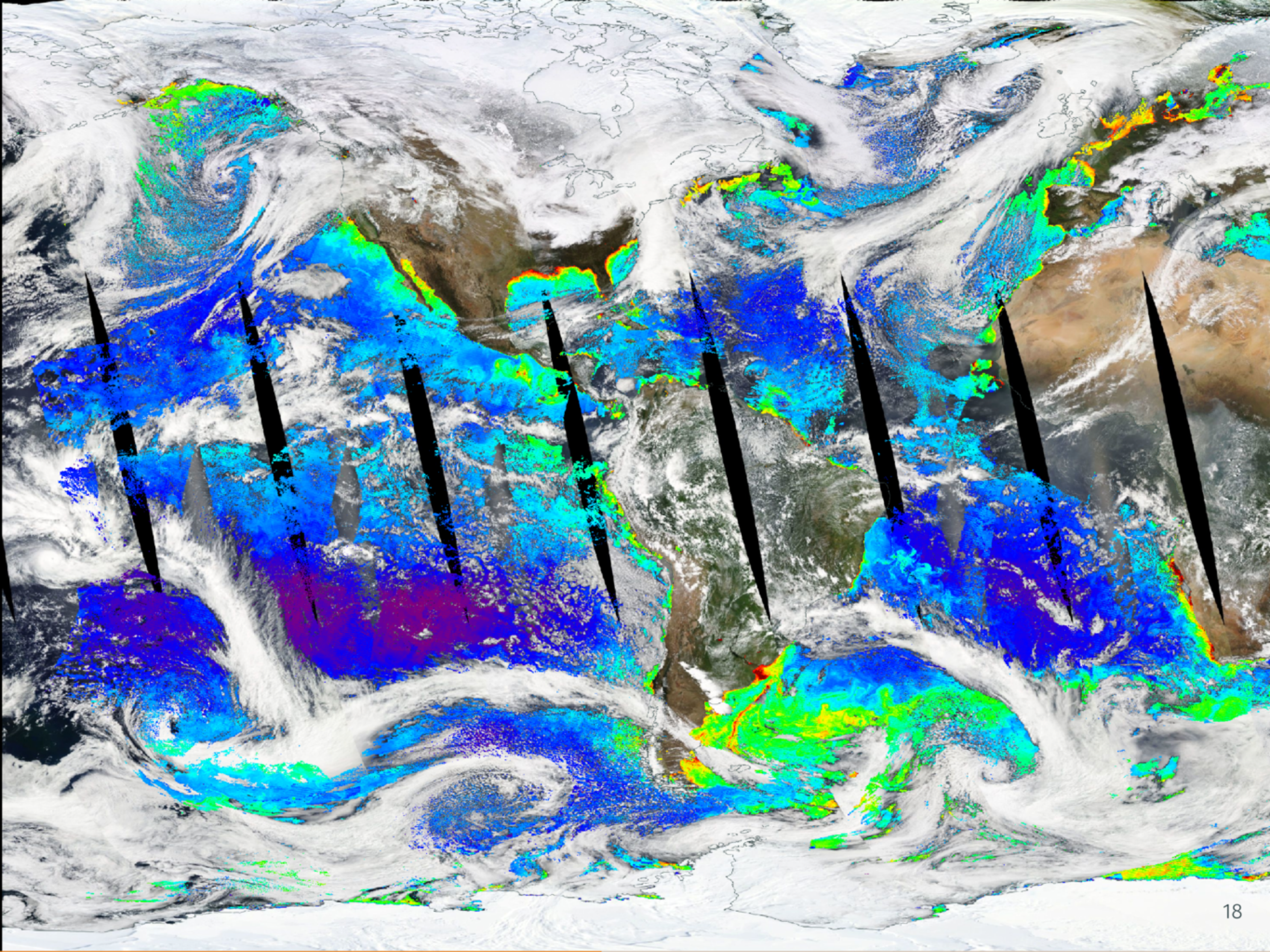


Potential temperature := the temperature if at the surface, i.e. accounting for pressure

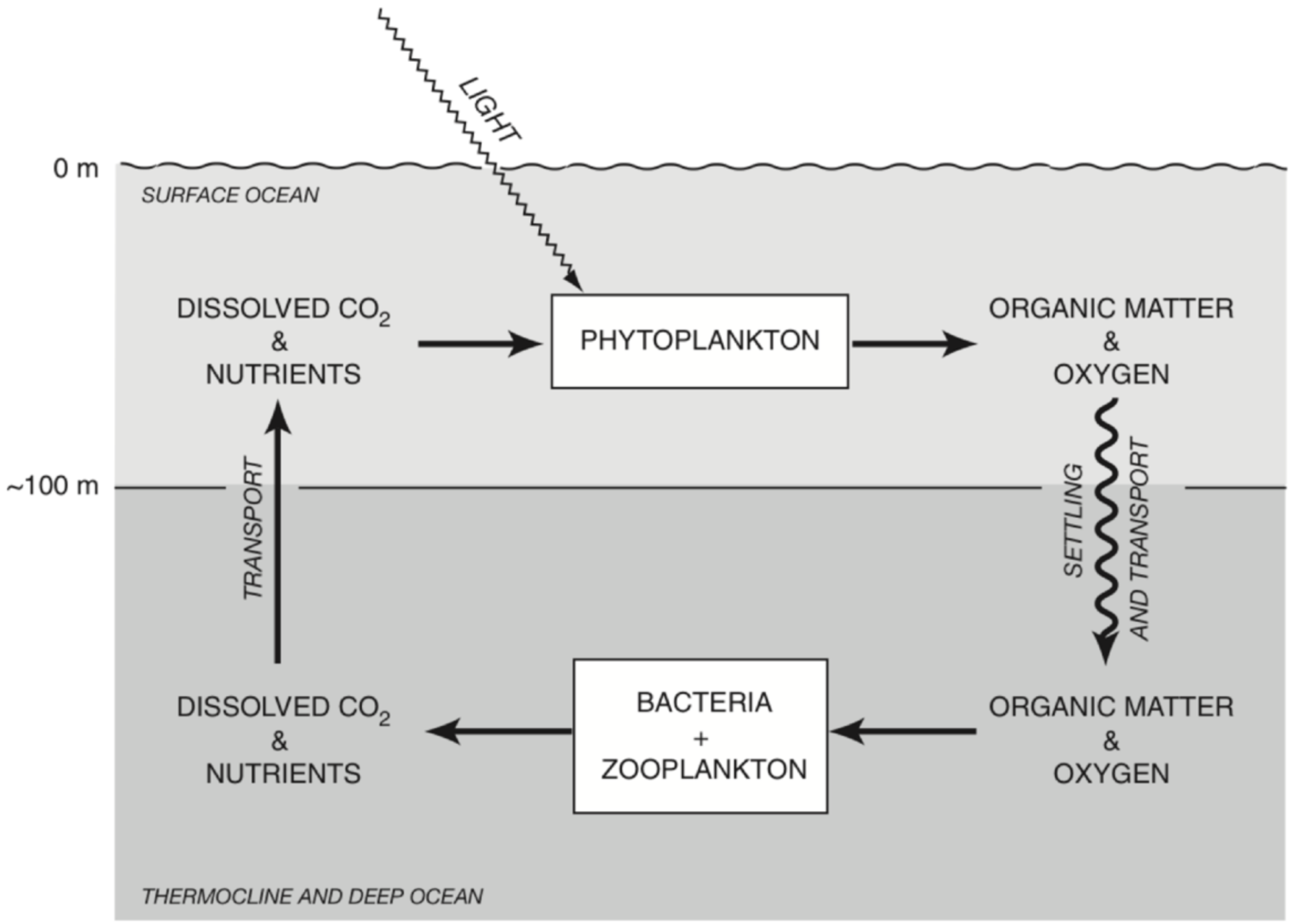
More realistic (cartoon of) ocean circulation



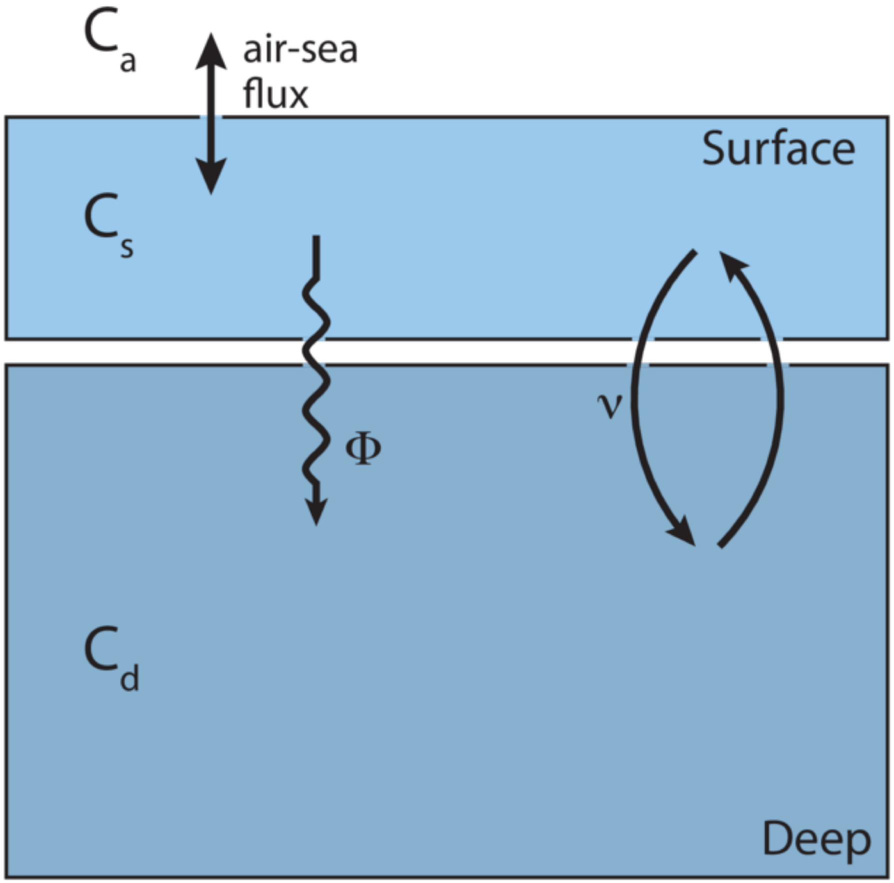
Williams & Follows, 2011



Marine carbon cycle summary



The vertical DIC gradient is enhanced by the biological pump



Mass balance (deep box)

$$V_d \frac{dC_d}{dt} = \Phi + \nu (C_s - C_d)$$

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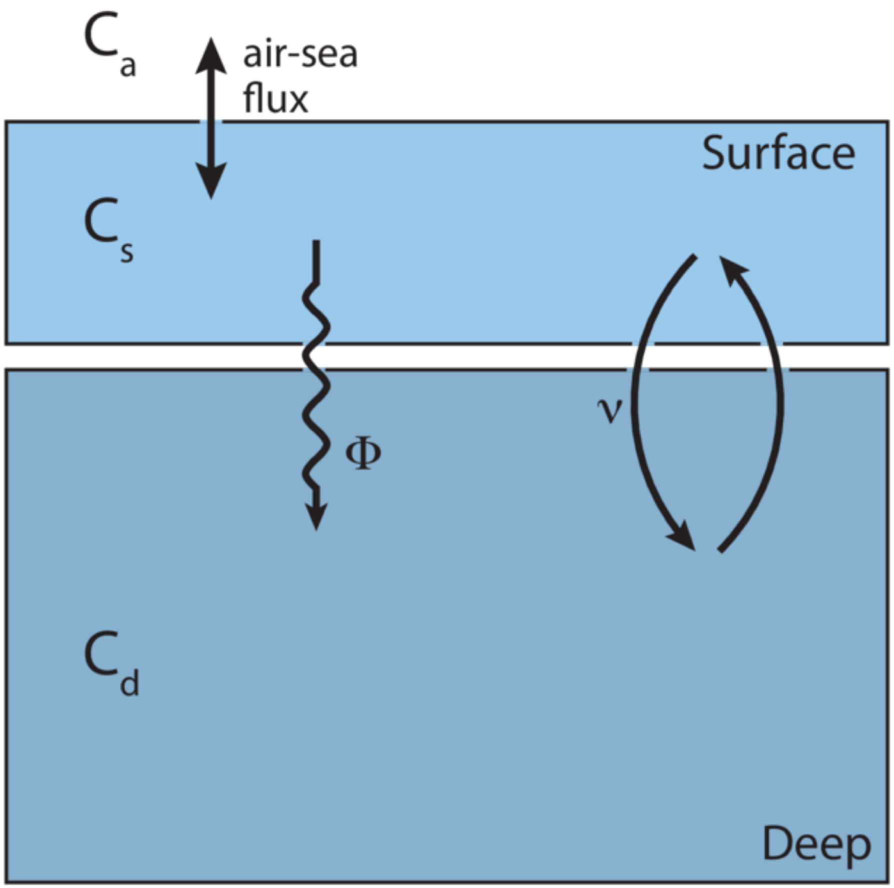


Mass balance (deep box)

$$V_d \frac{dC_d}{dt} = \Phi + \nu (C_s - C_d)$$

Steady-state

$$\Phi = \nu (C_d - C_s)$$

The vertical gradient

$$\frac{\Phi}{\nu} = (C_d - C_s)$$

where

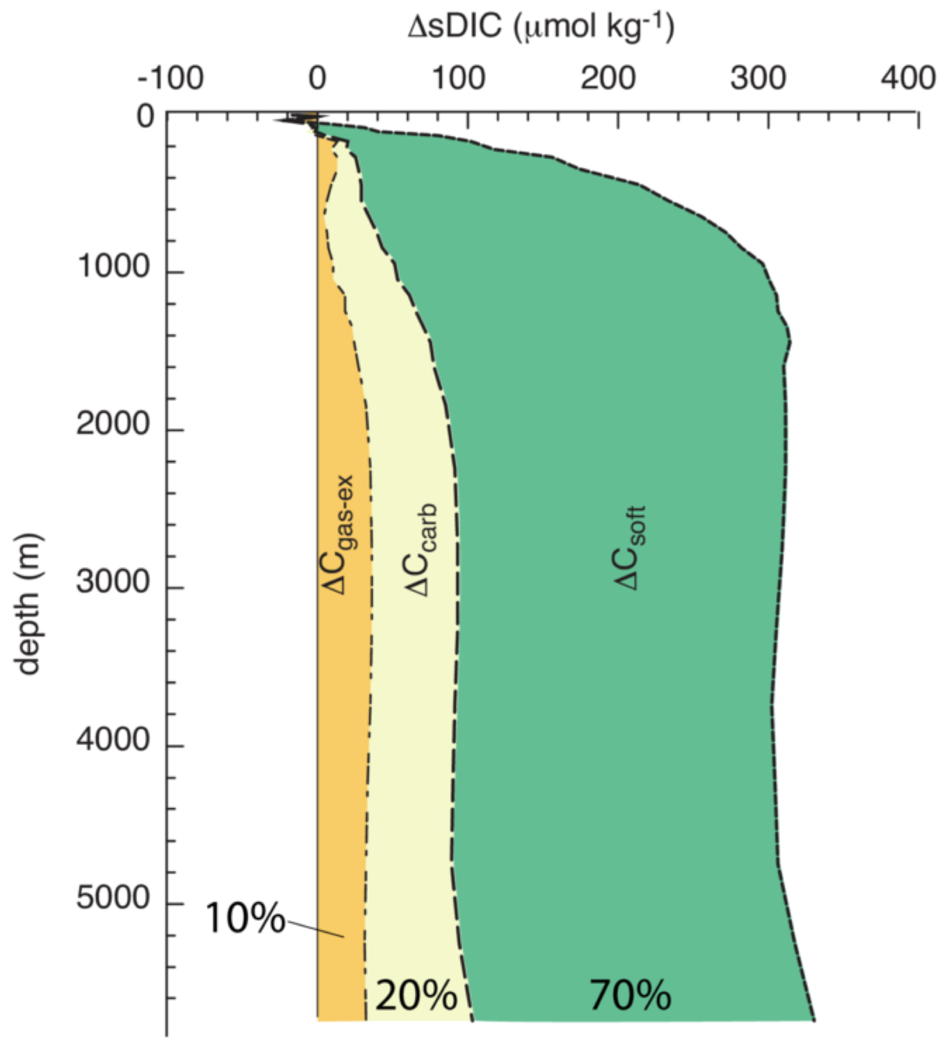
V_d = Volume of the deep box,

ν = Volume exchange rate,

Φ = Remineralization of sinking organic matter, and

$C_{s,d}$ = Concentrations in surface (s) and deep (d) boxes.

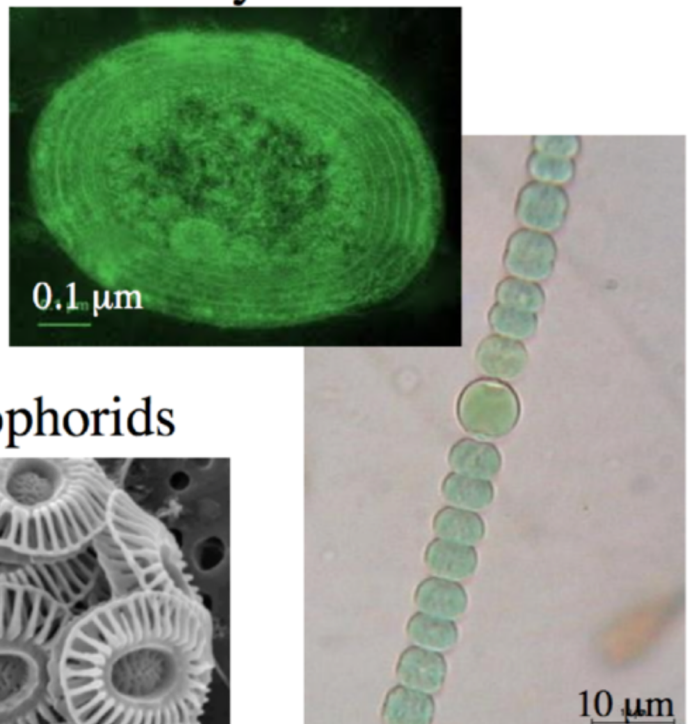
Contribution of carbon pumps to interior DIC



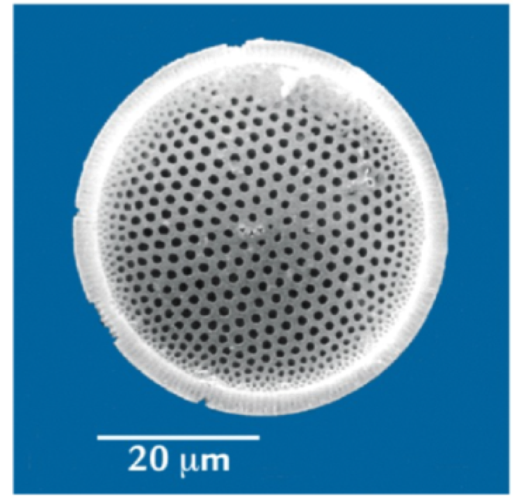
Sarmiento and Gruber 2006

Major oceanic primary producers

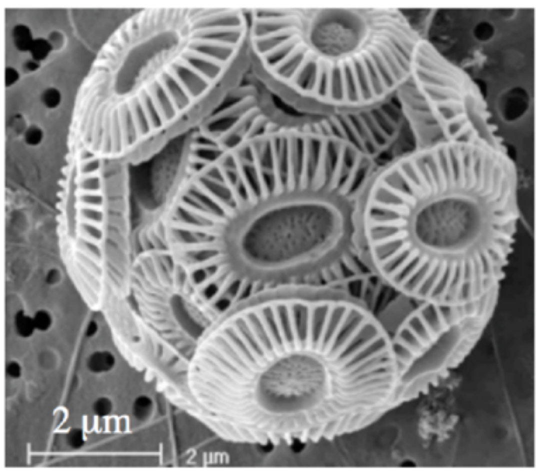
Cyanobacteria



Diatoms



Coccolithophorids



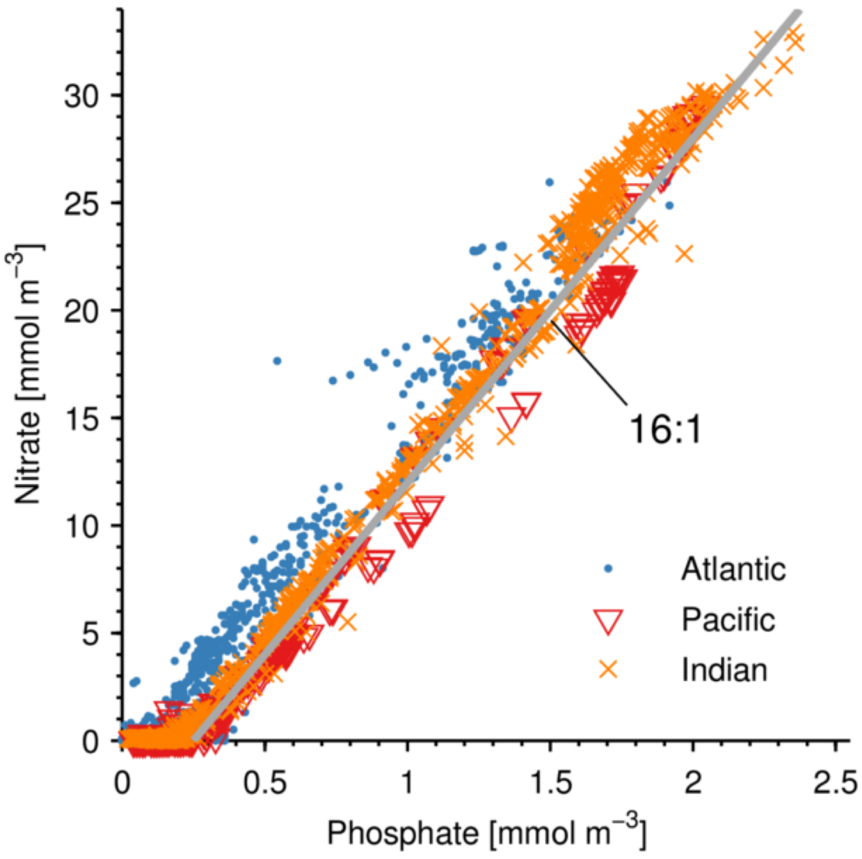
Dinoflagellates

Figure Sources: Ruddiman 3-17, VIMS

Organic matter production

$$\overbrace{106\,CO_2 + 16\,HNO_3 + H_3PO_4 + 78\,H_2O}^{\text{Inorganic constituents}} \rightleftharpoons \overbrace{C_{106}H_{175}O_{42}N_{16}P}^{\text{Organic matter}} + 150\,O_2$$

Relationship between NO_3^- and PO_4^{3-}



Nutrient utilization ratios

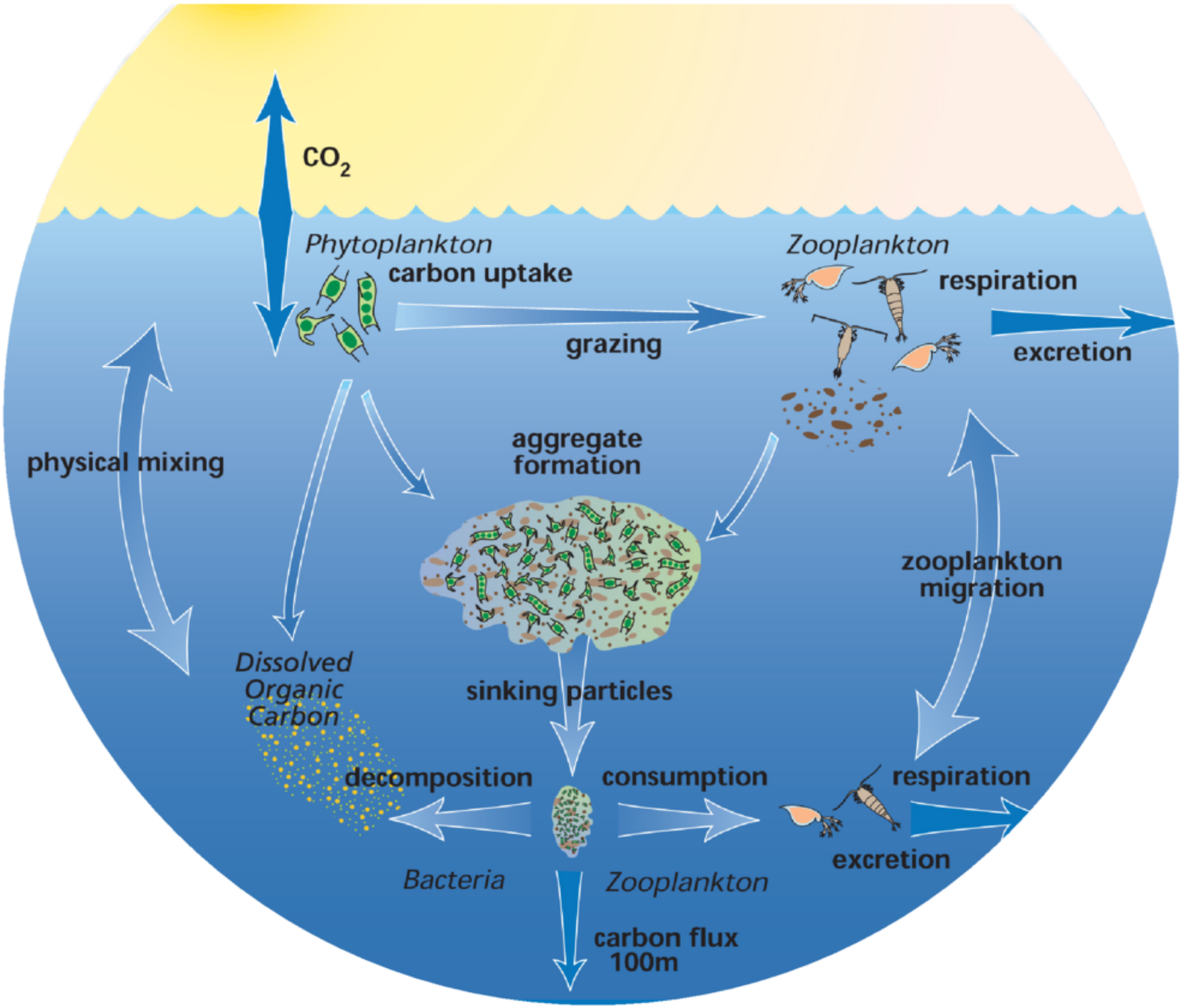
$C:N:P:O_2$ = 117:16:1:−170

Anderson & Sarmiento (1994)

P reservoir ($\int P\,dV$): geologically controlled slow turnover (∼50 ky).

N reservoir ($\int N\,dV$): biologically controlled fast turnover (∼2 ky).

The biological pump is a product of ecosystem function



U.S. JGOFS

Simple NPZ model

Phytoplankton

$$\frac{dP}{dt} = \mu_0 \left(\frac{N}{K_N + N} \right) \left(1 - e^{\alpha E/\mu_0} \right) P - g \left(\frac{P}{K_P + P} \right) Z - m_p P$$

Nutrient limitation — Light limitation — Grazing — Mortality

Zooplankton

$$\frac{dZ}{dt} = \gamma g \left(\frac{P}{K_P + P} \right) Z - m_z Z$$

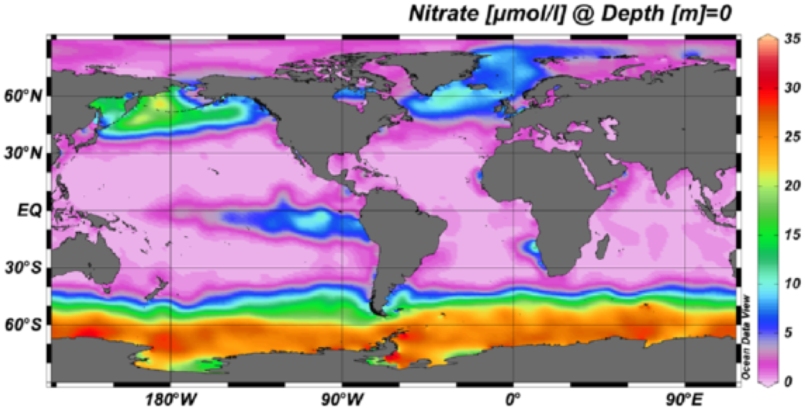
Nutrient

$$\frac{dN}{dt} = -\mu_0 \left(\frac{N}{K_N + N} \right) \left(1 - e^{\alpha E/\mu_0} \right) P + (1 - \gamma) g \left(\frac{P}{K_P + P} \right) Z + m_P P + m_z Z$$

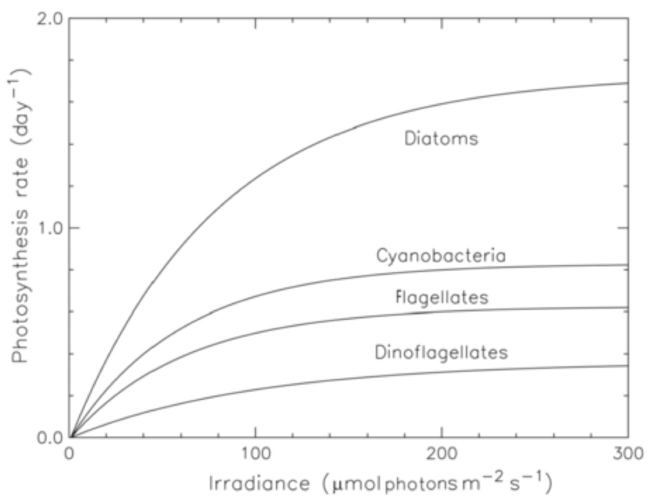
- Three coupled, ordinary differential equations
- Mass conserving
- 3 state variables (NPZ), 8 parameters ($\mu_0, K_N, \alpha, g, K_P, m_P, m_Z, \gamma$)

Plankton functional types (PFTs)

Environmental variability

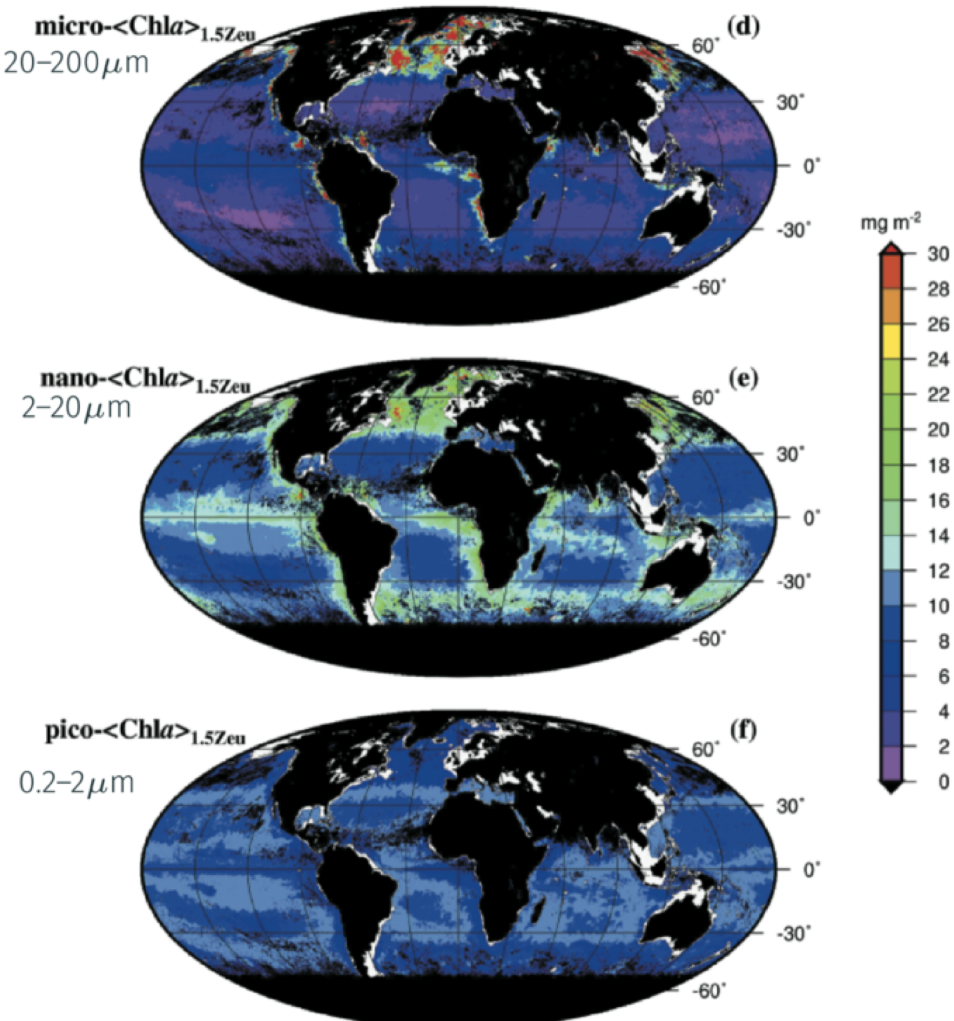


Physiological specialization



Le Quéré et al. 2005

Biogeography



Uitz et al. 2006

Plankton functional types (PFTs)

Definition

Conceptual grouping of phytoplankton species by ecological or biogeochemical function.

Examples

- Nitrogen fixers (e.g., Trichodesmium)
- Calcifiers (e.g., coccolithophores)
- Silicifiers (e.g., diatoms)
- Dimethyl sulfide (DMS) producers (e.g., Phaeocystis)

Robust prediction requires representation of key processes; e.g., export production may change with climate due to ecosystem shifts.

CESM Biogeochemical Element Model (BEC)

Doney et al., J. Mar. Systems, 2009

- 4 Plankton functional types
  - 3 autotrophs, 1 grazer
  - implicit calcifiers
  - explicit N fixers
- Nutrients: N, P, Si, Fe
- Fixed C:N stoichiometry
- Variable P:C, Fe:C, Si:C, & Chl:C
- Implicit treatment of sinking detritus
- Dynamic Fe cycle with prognostic Fe-binding ligand

References:

Moore et al., *Deep Ses Res.*, 2002.

Moore, Doney, & Lindsay, *GBC*, 2004.

Moore & Braucher, *Biogeosciences*, 2008.

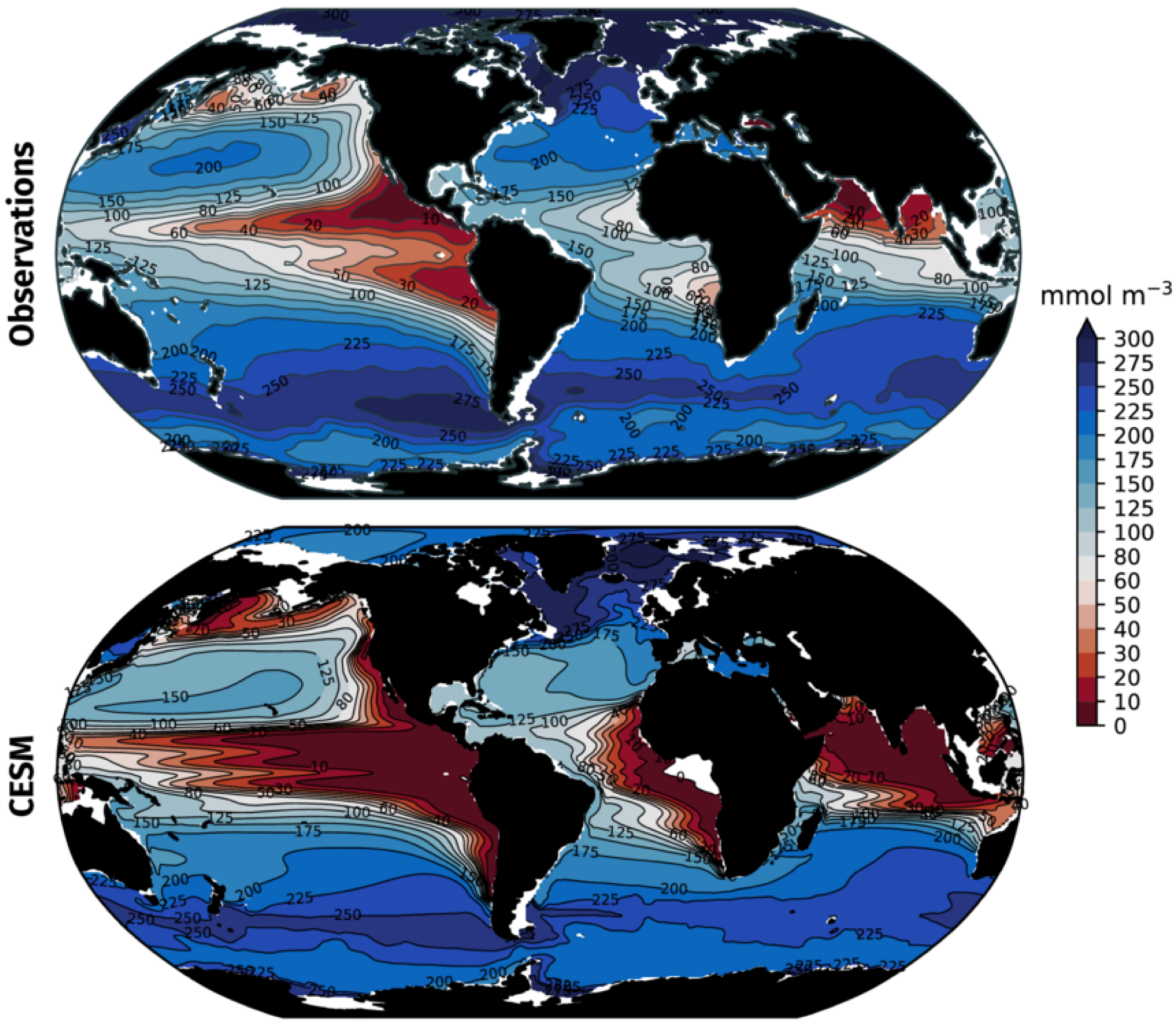
Moore et al., *J. Climate*, 2013.

Known gaps in CESM ocean biogeochemistry

- Calcification & open ocean $CaCO_3$ dissolution rates are independent of saturation state (Ω);
- Riverine inputs of BGC tracers are prescribed;
- C, N, P, Si, $CaCO_3$ buried in sediments are lost from the system;
- No treatment of BGC in sea-ice;
- No explicit particulate organic matter pool;
- No explicit heterotrophic bacteria;
- Focus on lower trophic levels; limited diversity.

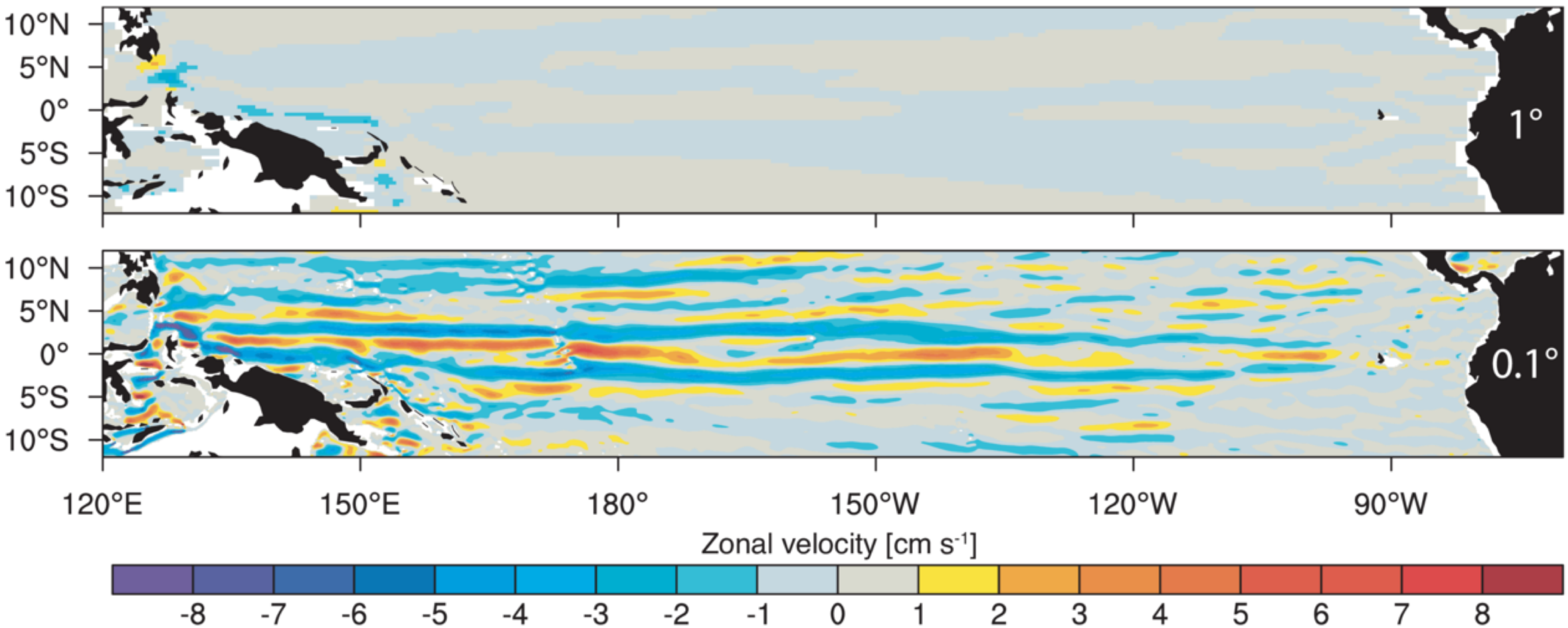
A persistent bias in Earth system models: Extensive OMZs

World Ocean Atlas Comparison: Thermocline (400–600 m) dissolved oxygen



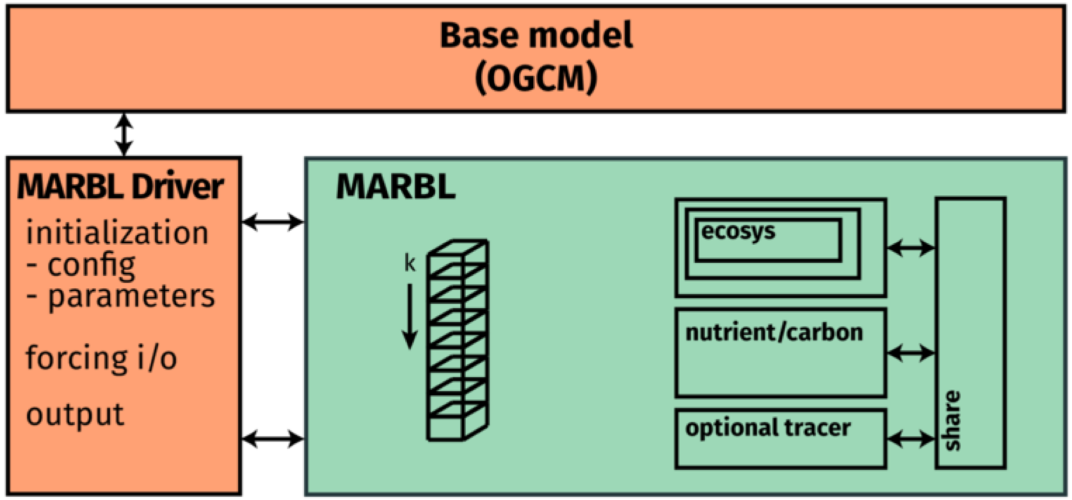
Model resolution determines ventilation dynamics

Simulated zonal velocity at 1000 m



CESM ocean biogeochemistry implementation: MARBL

The Marine Biogeochemistry Library (github.com/marbl-ecosys/MARBL)

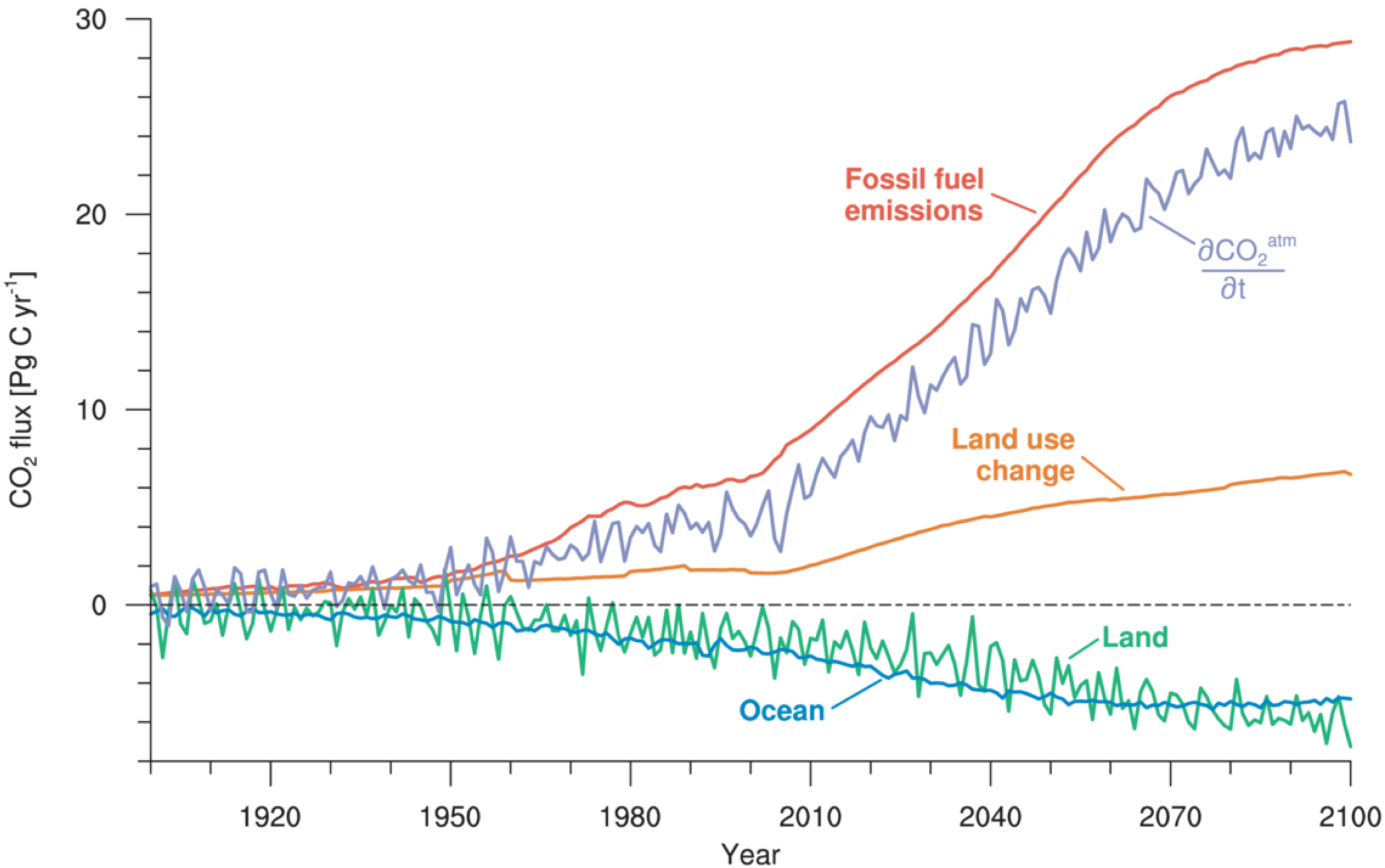


$$\frac{\partial \varphi}{\partial t} + \nabla \cdot (\vec{u}\varphi) - \nabla \cdot (K \nabla \varphi) = J(\varphi)$$

- MARBL is a GCM-independent implementation of ocean biogeochemistry;
- Ecosystem configuration is flexible; includes optional tracer packages (i.e., ^{13}C);
- Matlab and Python interface (under development).

Coupled carbon: Emissions-forced prognostic budget

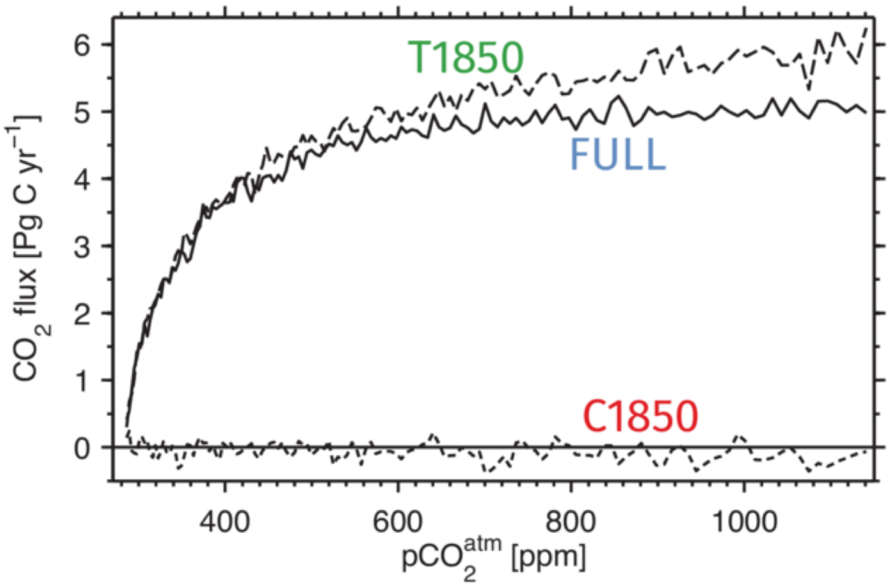
CESM1(BGC): historial $\rightarrow$ RCP8.5

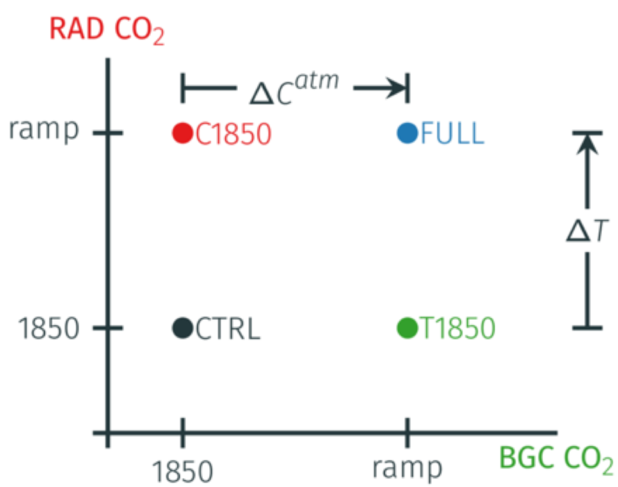


Hurrell et al. 2013

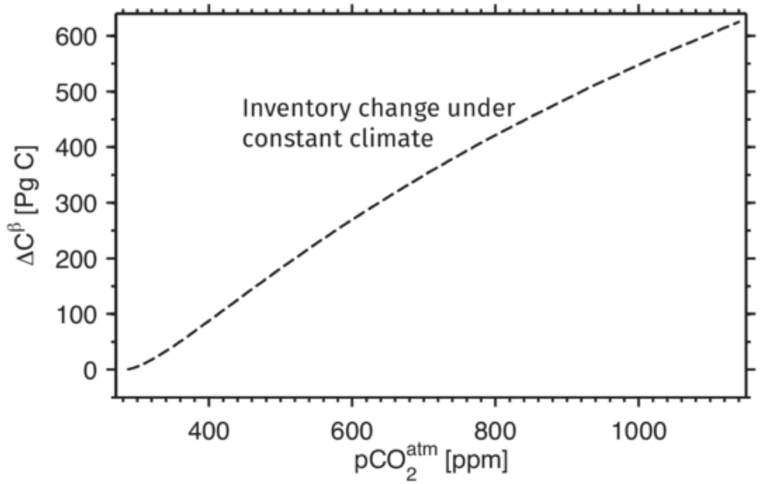
CESM1 results: Carbon-climate feedbacks under 1% yr^{-1} ramping CO_2

Air-to-sea flux: anomaly timeseries

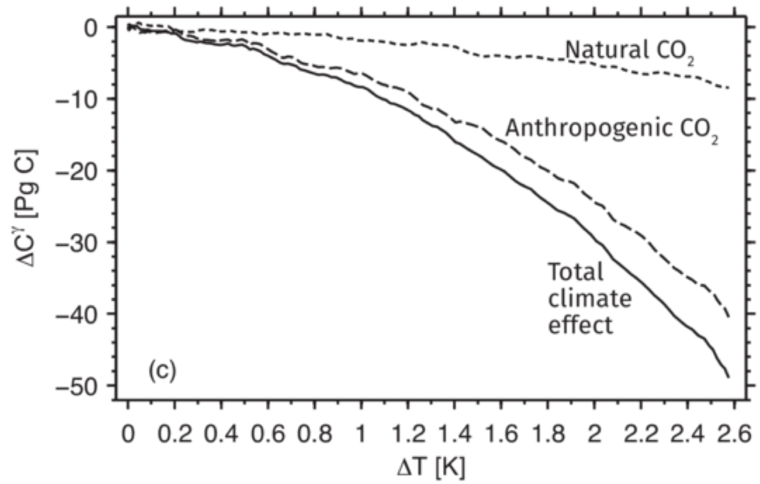




Ocean uptake under rising CO_2 (T1850)

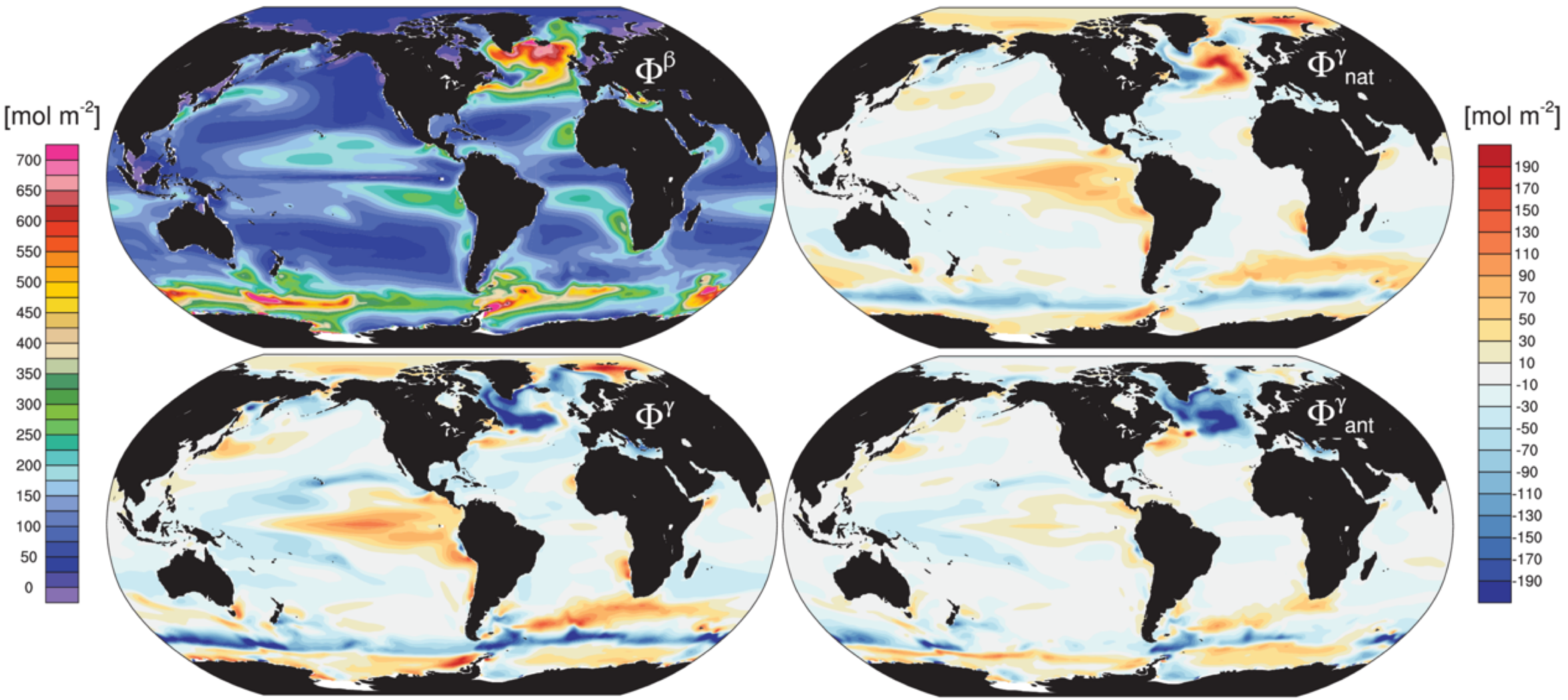


Climate-driven reductions in CO_2 uptake



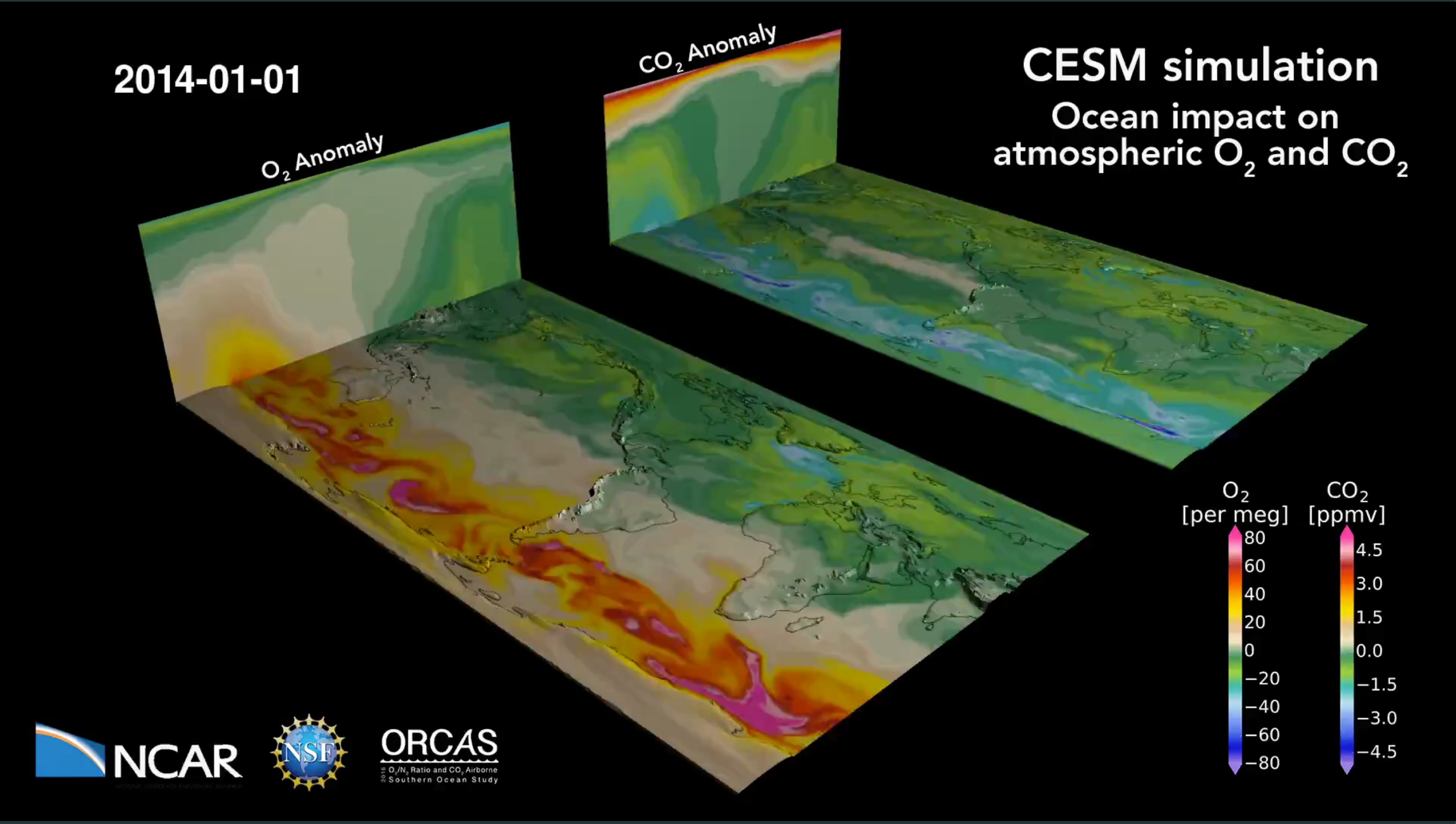
Spatially variable feedbacks

Time-integrated air-to-sea CO_2 flux components



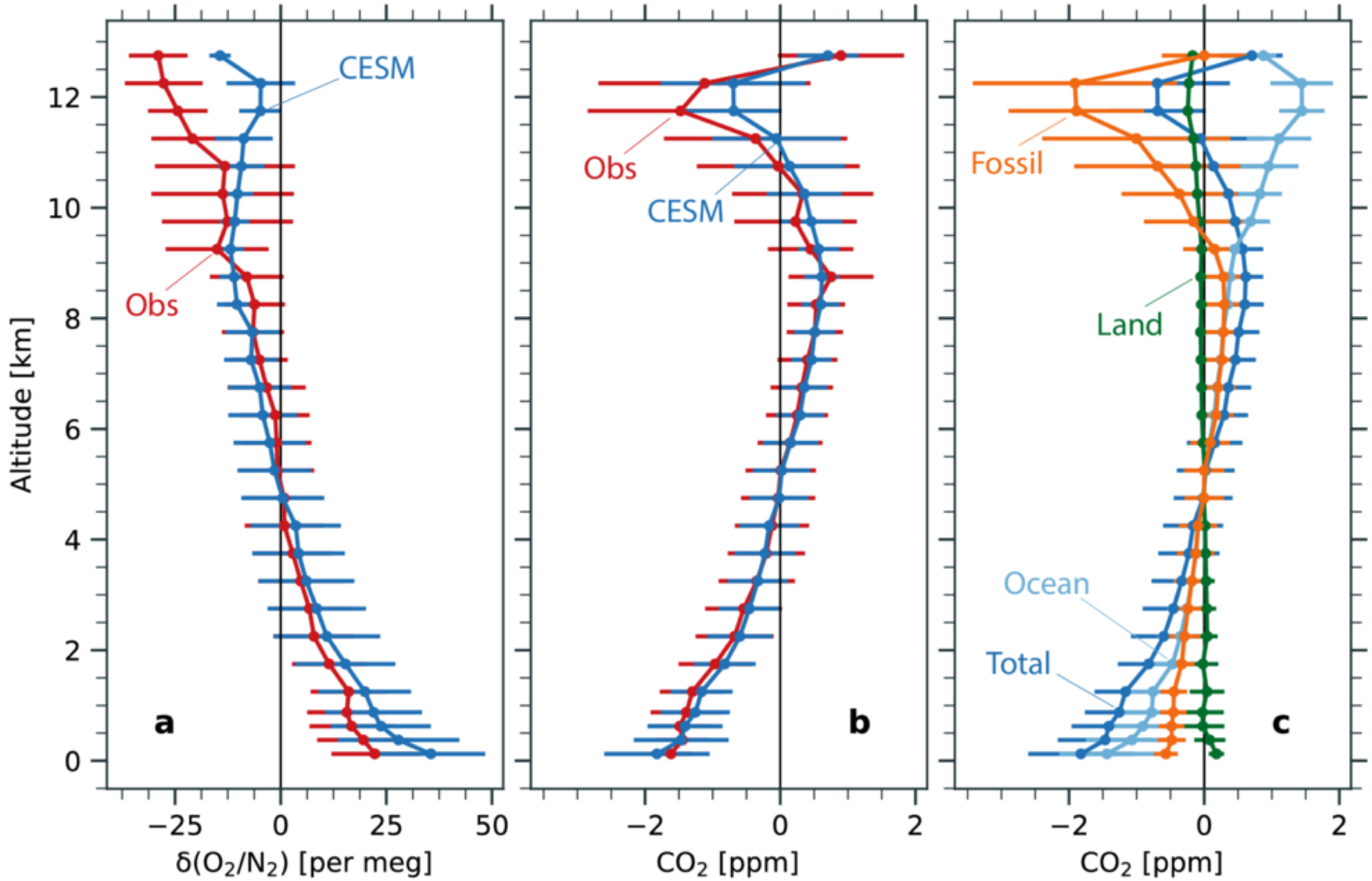
positive := down

Simulated O_2 and CO_2 distributions



Comparison to aircraft observations over the Southern Ocean

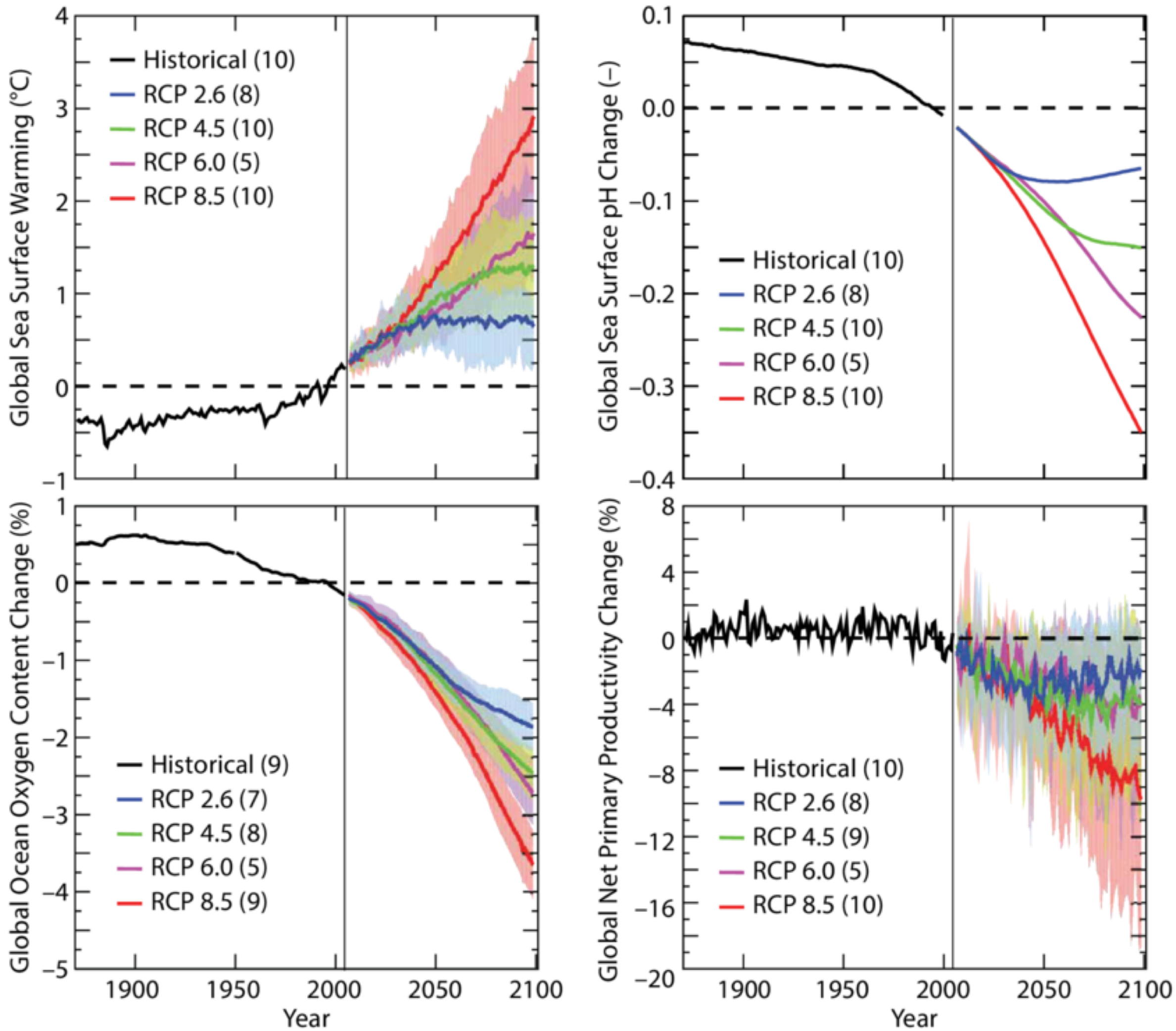
Altitude-bin-averaged vertical profiles, normalized to >12 km



- Model overestimates O_2 gradient: implies wrong balance of forcing mechanisms.

Stephens, Long, et al. 2018

CMIP5 multi-model global-mean projections: multiple stressors



Doney, Bopp, & Long, 2014

* *Gruber, 2011*

Summary

CO_2 in seawater enters a series of acid-base equilibria reactions, increasing the total dissolved inorganic carbon (DIC) concentration above that of $CO_{2,aq}$.

The ocean absorbs anthropogenic CO_2 at a rate governed by ocean ventilation timescales. (The ocean's ability to continue to absorb CO_2 decreases as concentrations increase.)

The biological pump transfers carbon to depth, increasing the total carbon storage of the ocean and coupling carbon and nutrient cycles; it is a product of ecosystem function.

Anthropogenic CO_2 and warming are likely to severely impact marine ecosystems and biogeochemistry:

- Reduction in net primary productivity;
- Deoxygenation & warming;
- Reduced carbon uptake, pH decline.

Questions?

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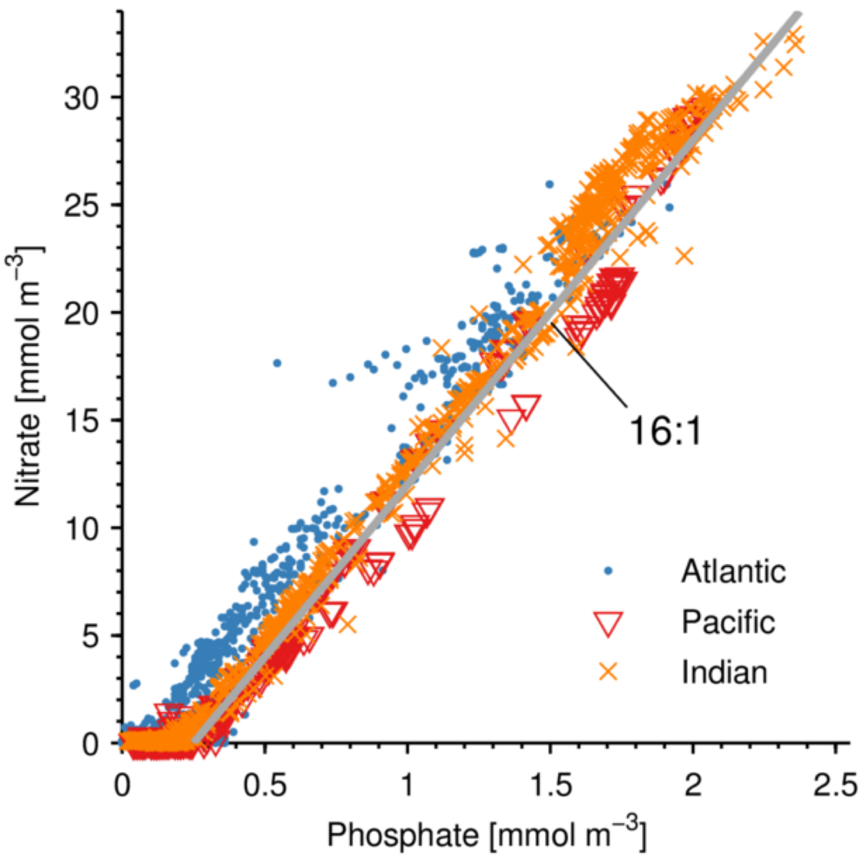
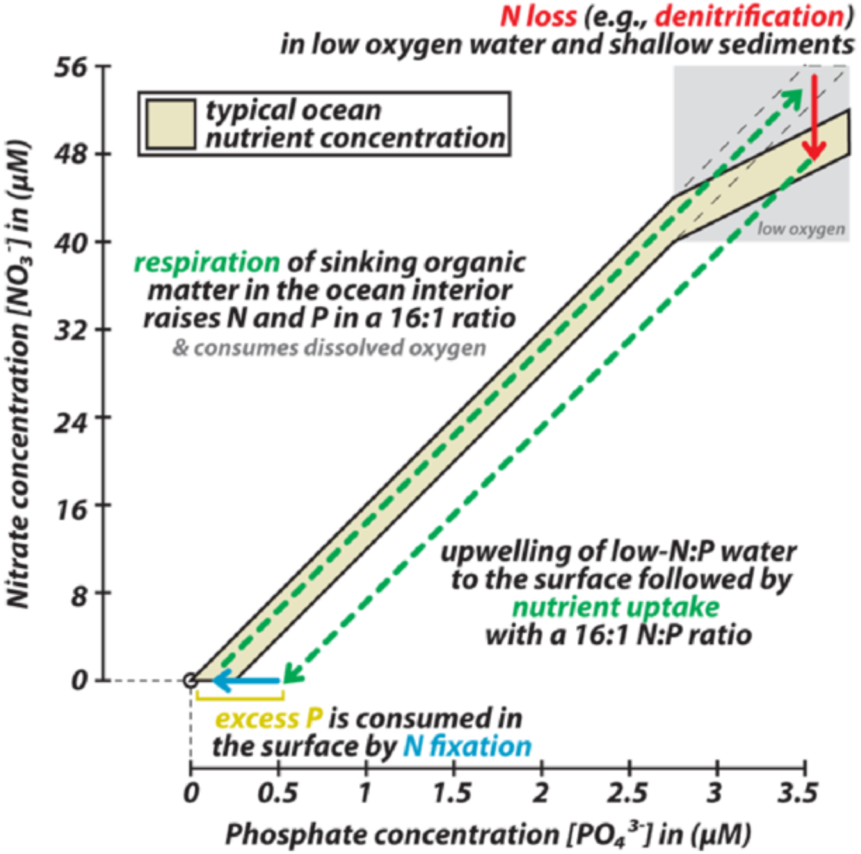
Organic matter production

Inorganic constituents → Organic matter

$$106\,CO_2 + 16\,HNO_3 + H_3PO_4 + 78\,H_2O \rightleftharpoons C_{106}H_{175}O_{42}N_{16}P + 150\,O_2$$

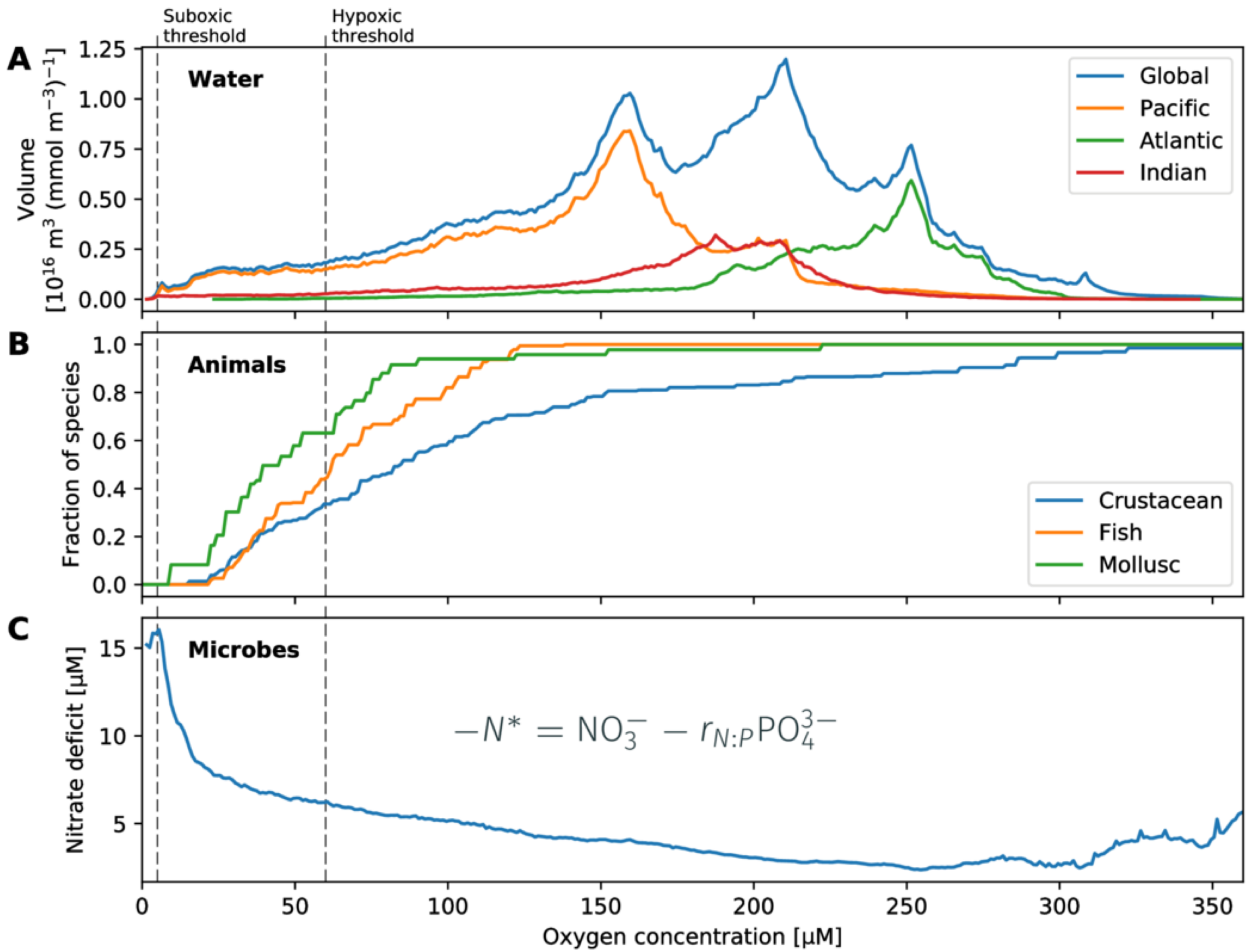
Relationship between NO_3^- and PO_4^{3-}





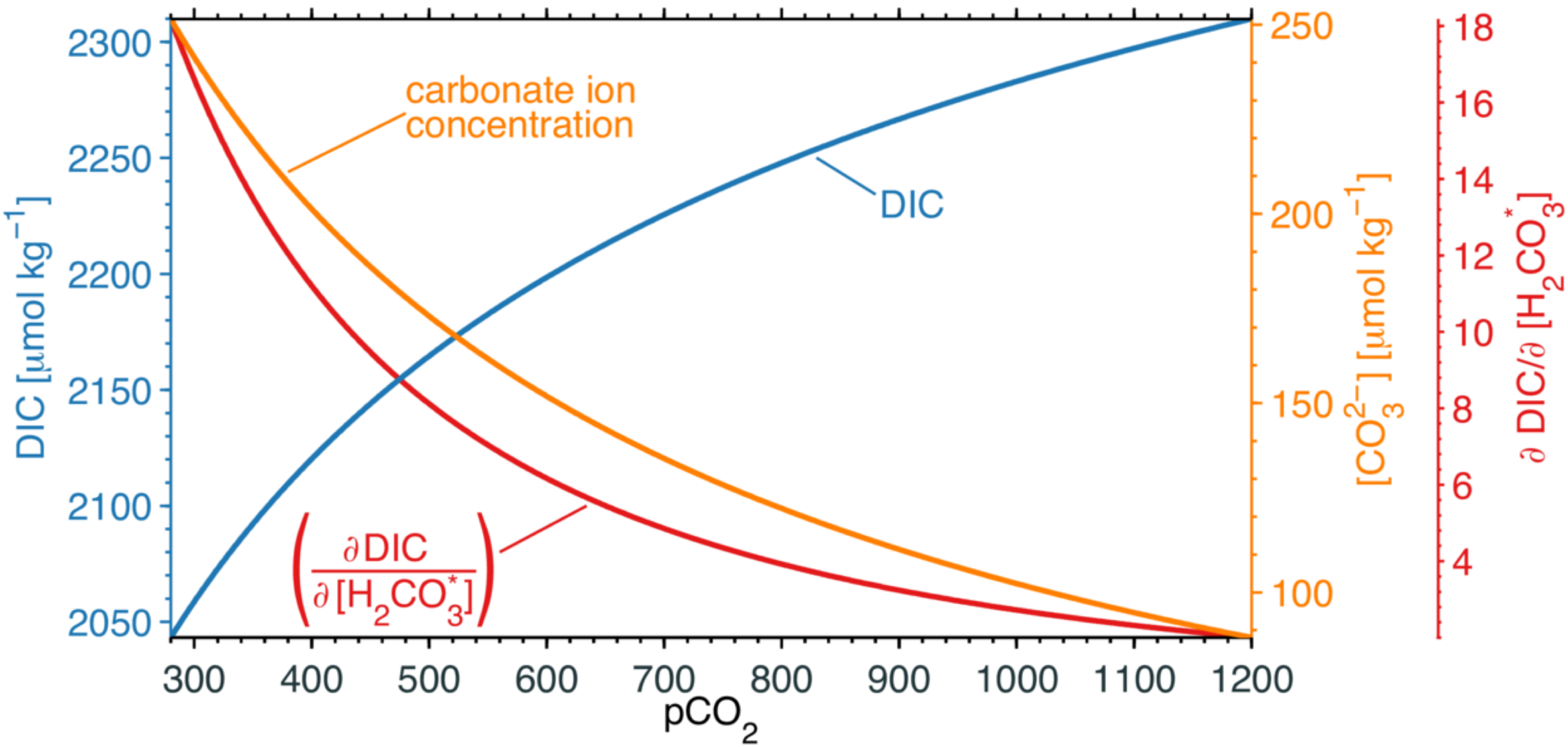
Sigman 2012

Oxygen is a fundamental environmental constraint



One-box ocean model: Equilibration to rising pCO_2^{atm}

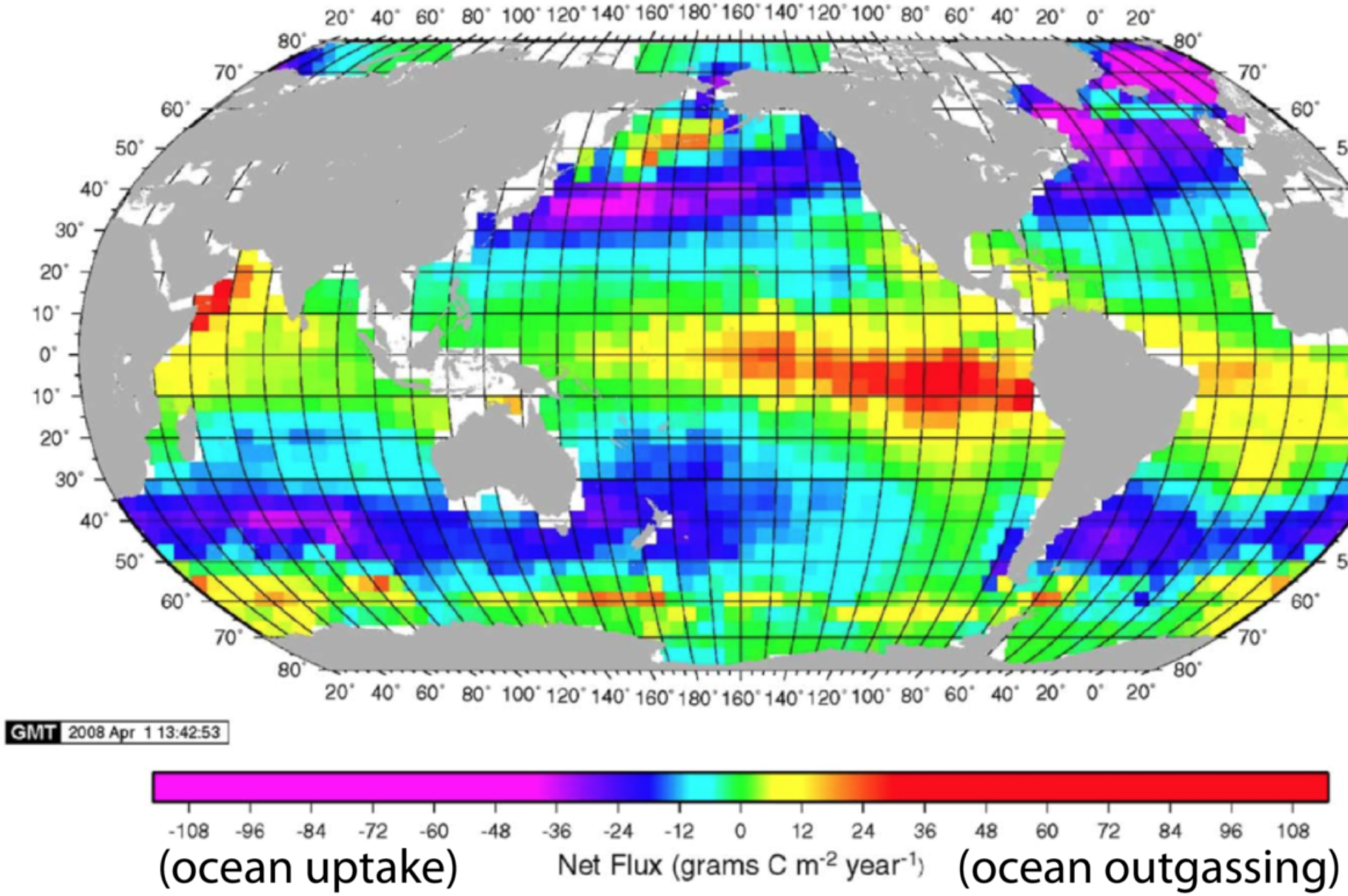
$$H_2CO_3^* + CO_3^{2-} \rightleftharpoons 2HCO_3^-$$



$T = 20°C$; $S = 35$; $Alk = 2400\ \mu eq\ kg^{-1}$

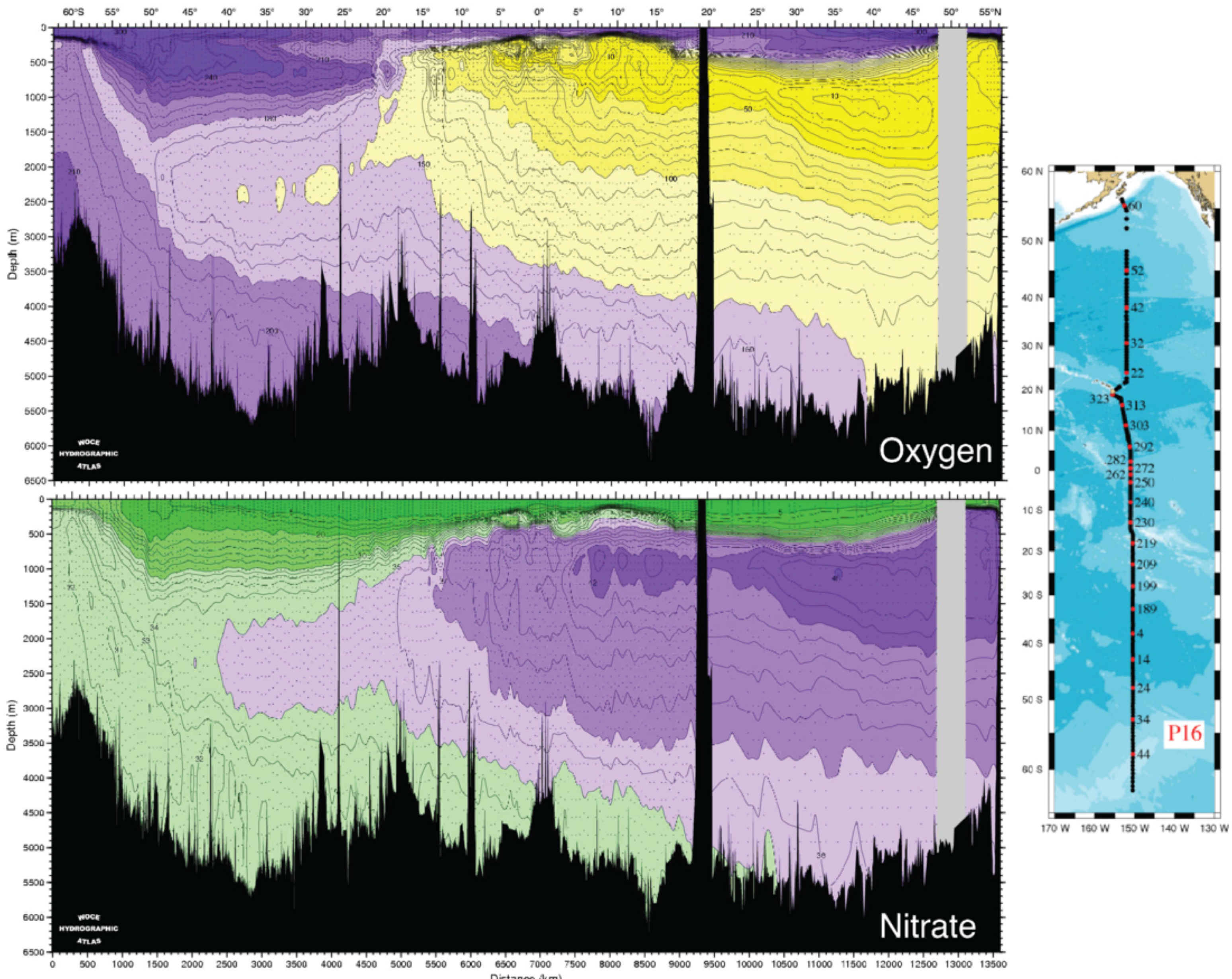
Air-sea CO_2 gas flux

Mean annual air-sea flux

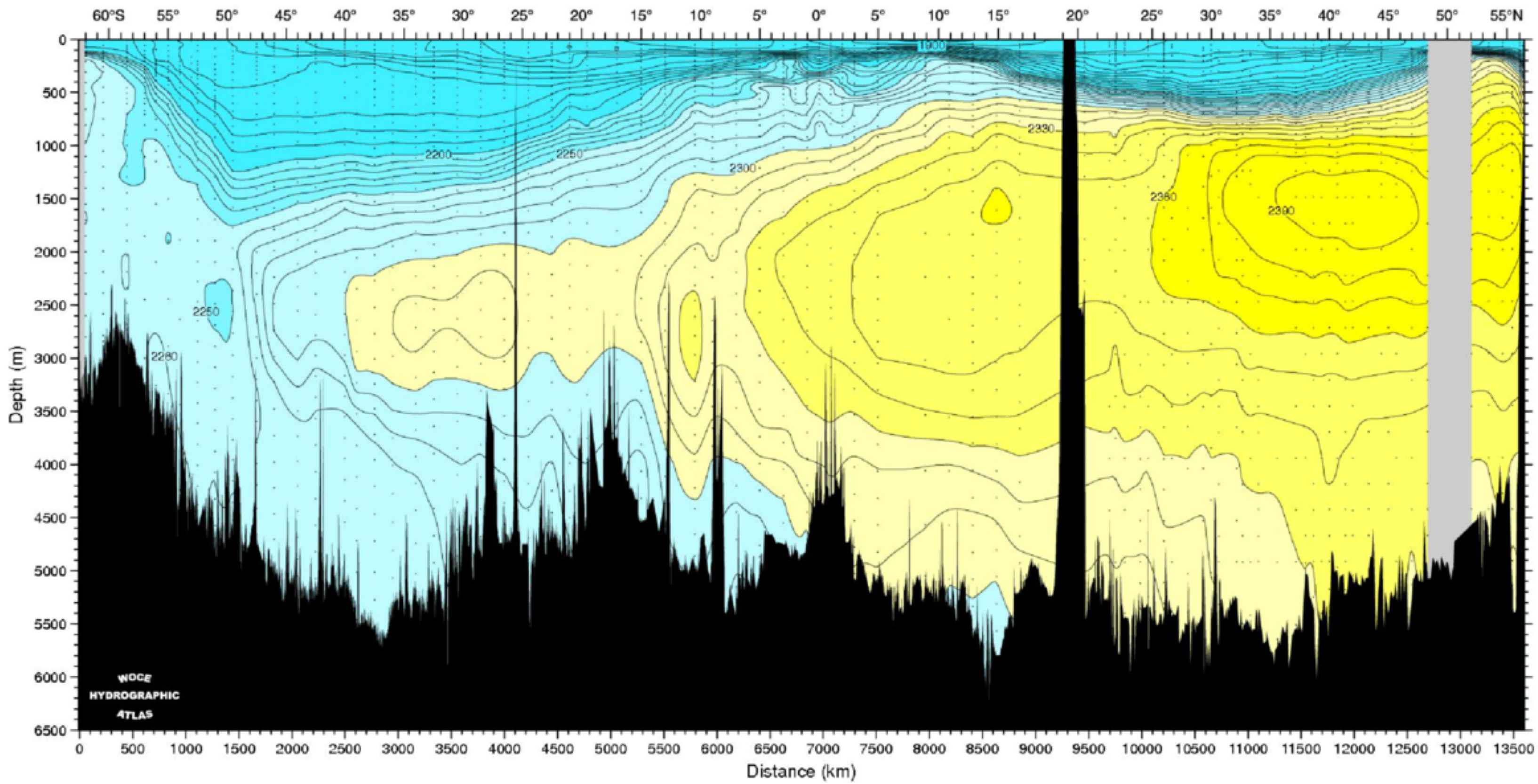


Takahashi et al., 2009

Properties along P16: dissolved oxygen and nitrate



Properties along P16: Dissolved inorganic carbon (DIC)



$$DIC = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$$