2013 NCAR ASP
Graduate Student Colloquium

Ocean carbon biogeochemistry: thermodynamics, carbon chemistry, gas exchange

Matthew C. Long

Climate and Global Dynamics Division
National Center for Atmospheric Research

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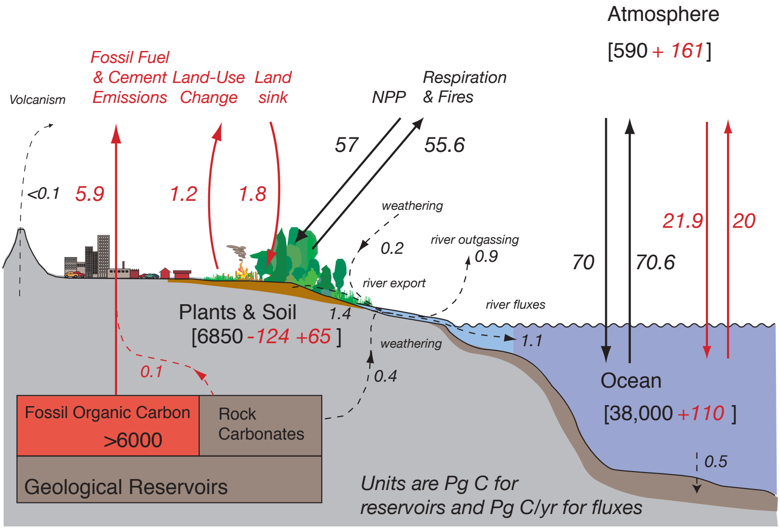
The ocean contains the largest active C reservoir on Earth

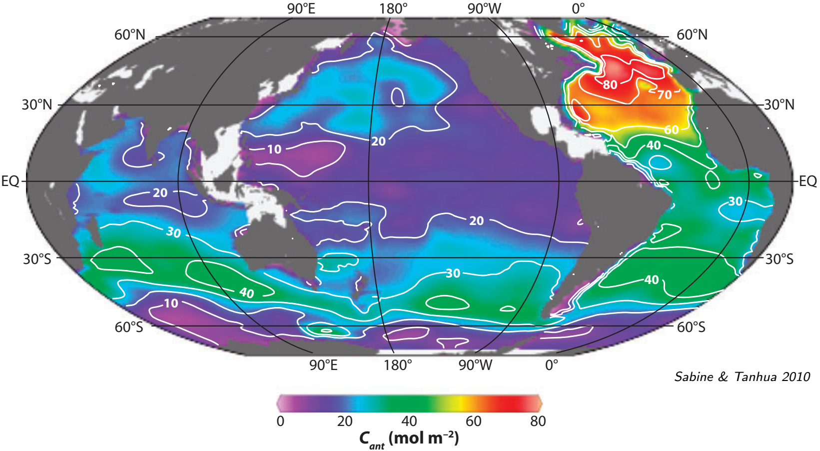
The global carbon budget (c. 1990s)



Sabine, Heiman et al. 2004

The ocean has absorbed 25–30% of anthropogenic CO_2 to date

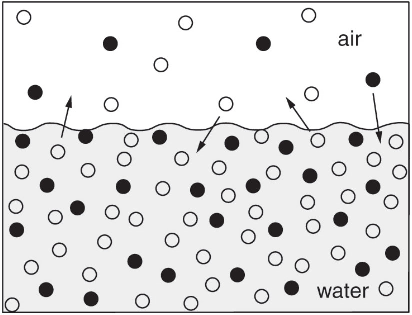
Ocean C_{ant} inventory (1990s)



Sabine & Tanhua 2010

Definitions for soluble gases

Air-sea partitioning of soluble gases



Williams and Follows 2011

Definitions (for generic soluble gas A)

Mixing ratio

$$\chi_A = \frac{N_A}{\sum_{i=1}^{n} N_i}$$

where N_i = number of moles of gas i.

Partial pressure

$$p_A = \chi_A \cdot P_{total}$$

and

$$P_{total} = \sum_{i=1}^{n} p_i \quad \text{(Dalton's law)}$$

Solubility

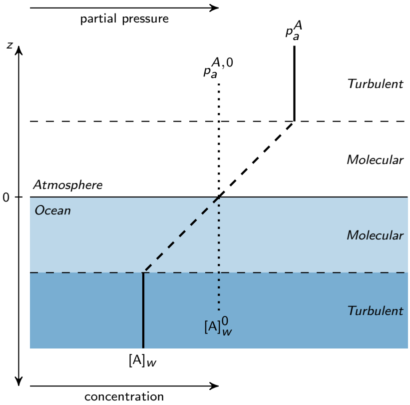
$$S_A \equiv \frac{[A]^{equilibrium}}{p_A} \quad \text{(Henry's law)}$$

where S_A is the solubility of A (mol m^{-3} atm^{-1}) and $[A]^{equilibrium}$ is the equilibrium concentration in solution (mol m^{-3}).

Fugacity

The 'effective' partial pressure, corrected to account for non-ideality. For CO_2, the correction is typically $< 1\%$.

Gas exchange



Sarmiento & Gruber 2006

Parameterizing gas exchange

The air-sea flux of a slightly soluble gas, A:

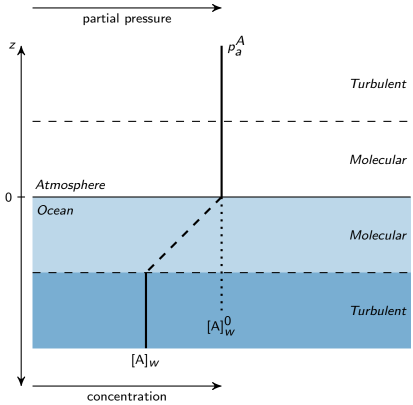
$$\Phi = k_w \cdot ([A]_w - [A]_{eq})$$

or in terms of partial pressure

$$\Phi = k_w \cdot S_A \cdot (p_w^A - p_a^A)$$

where k_w is the gas transfer velocity.

Gas exchange



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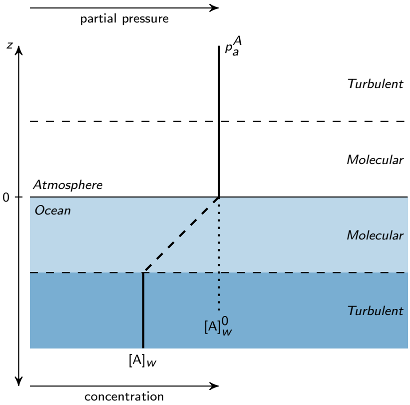

Sarmiento & Gruber 2006

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where k_w is the gas transfer velocity.

Parameterization of k_w are empirical, but based on a conceptual model involving aqueous hydrodynamics near the air-sea interface.

k_w is usually parameterized as function of wind speed U

$$k = aSc^{-n}U^m$$

where $m > 1$ and $1/2 \leq n \leq 2/3$.

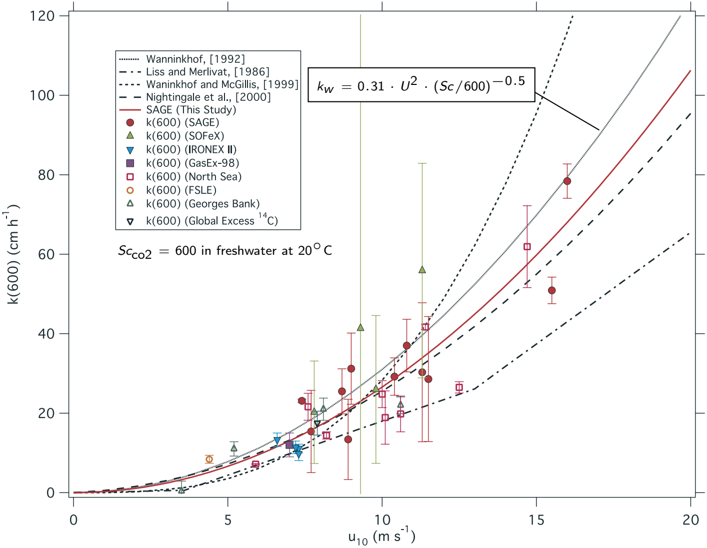
Dependence on the Schmidt number, $Sc = \nu/D$, where

ν is the kinematic viscosity of water, and
D is the molecular diffusivity,

allows k_w measurements to be translated for different gases and represents controls on the thickness of the stagnant film.

Gas exchange

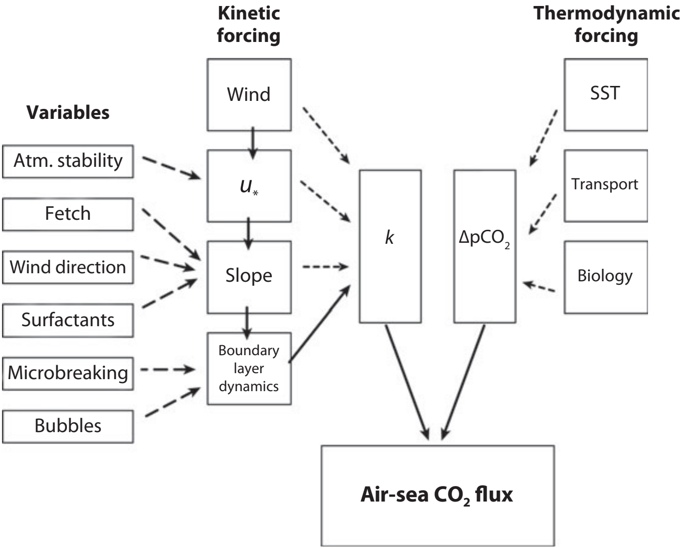
Short-term wind-speed dependent gas exchange parameterizations



Ho et al. 2006

Gas exchange

Factors affecting air-sea CO_2 exchange

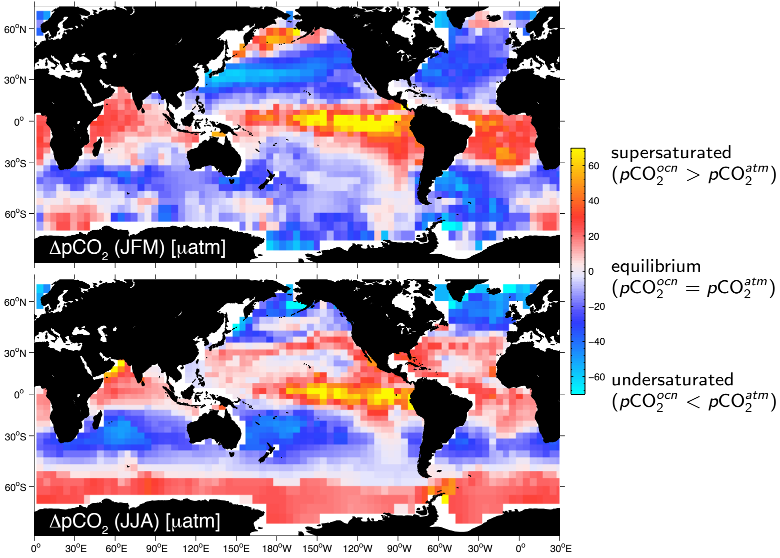


Wanninkhof et al. 2009

Sea-air pCO_2 difference

$(\Delta pCO_2 = pCO_2^{ocn} - pCO_2^{atm})$

Climatological ΔpCO_2



Takahashi et al. 2009

Inorganic carbon chemistry

Reactions in solution

The following series of equilibria occur when carbon dioxide dissolves in water:

$$CO_{2,g} \rightleftharpoons CO_{2,aq} \tag{1}$$

$$CO_{2,aq} + H_2O \rightleftharpoons H_2CO_3 \tag{2}$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \tag{3}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \tag{4}$$

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It is difficult to analytically distinguish between $CO_{2,aq}$ and H_2CO_3, therefore it is common to use

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

thus (1–3) become

$$CO_{2,g} + H_2O \rightleftharpoons H_2CO_3^* \tag{5}$$

$$H_2CO_3^* \rightleftharpoons H^+ + HCO_3^- \tag{6}$$

Dynamic equilibrium

Kinetic equation and equilibrium

$$H_2CO_3^* \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} H^+ + HCO_3^-$$

Kinetic equation

$$\frac{d[H_2CO_3^*]}{dt} = -k_{+1}[H_2CO_3^*] + k_{-1}[HCO_3^-][H^+]$$

with rate constants
k_{+1} (s^{-1}) for the forward reaction and
k_{-1} ($(\text{mol kg}^{-1})^{-1}\ s^{-1}$) for the reverse.

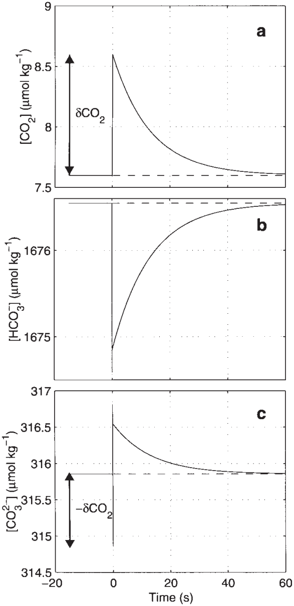
Equilibrium

At equilibrium, $\frac{d[H_2CO_3^*]}{dt} = 0$.

Therefore

$$\frac{[H^+][HCO_3^-]}{[H_2CO_3^*]} = \frac{k_{+1}}{k_{-1}} = K_1$$

Relaxation timescale of carbonate species following a perturbation in CO_2 (δCO_2). } →



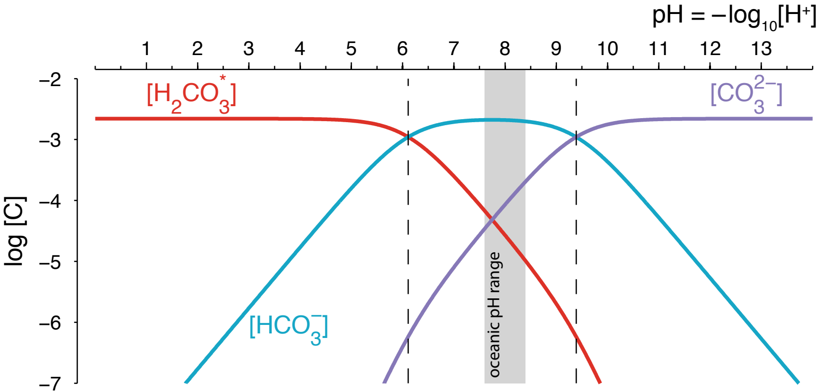
Zeebe and Wolf-Gladrow 2001

Inorganic carbon chemistry

Equilibrium relationships

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

Carbonate speciation



Inorganic carbon chemistry

Dissolved inorganic carbon (total CO_2)

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

Alkalinity

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

Additional reactions

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

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

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

Inorganic carbon chemistry

Unknowns

$p\mathrm{CO_2}$, $[\mathrm{H_2CO_3^*}]$, $[\mathrm{HCO_3^-}]$, $[\mathrm{CO_3^{2-}}]$, $[\mathrm{H^+}]$, $[\mathrm{OH^-}]$, $[\mathrm{B(OH)_4^-}]$, $[\mathrm{H_3BO_3}]$, Alk, DIC

Equations

Along with the definitions of Alk and DIC, we have

$$K_0 = \frac{[\mathrm{H_2CO_3^*}]}{p\mathrm{CO_2}},\ K_1 = \frac{[\mathrm{H^+}][\mathrm{HCO_3^-}]}{[\mathrm{H_2CO_3^*}]},\ K_2 = \frac{[\mathrm{H^+}][\mathrm{CO_3^{2-}}]}{[\mathrm{HCO_3^-}]},$$
$$K_w = [\mathrm{H^+}][\mathrm{OH^-}],\ K_B = \frac{[\mathrm{H^+}][\mathrm{B(OH)_4^-}]}{[\mathrm{H_3BO_3}]},$$

and total boron conservation, yielding constant proportionality to salinity

$$\mathrm{B}_T = [\mathrm{B(OH)_4^-}] + [\mathrm{H_3BO_3}] = c \cdot S$$

yielding 8 equations; thus, the carbonate system can be solved by specifying any two of the 10 unknowns.

Inorganic carbon chemistry

Modeling ocean carbon

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, gas exchange, freshwater inputs).

Inorganic carbon chemistry

Modeling ocean carbon

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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. $pCO_2 = \frac{[H_2CO_3^*]}{K_0} \rightarrow$ gas exchange $= f(\Delta pCO_2)$.

Surface ocean distributions

Controls on pCO_2

Direct solubility effect

$$pCO_2 = \frac{[H_2CO_3^*]}{K_0}$$

Indirect chemical effects

$$pCO_2 = \frac{K_2}{K_0 \cdot K_1} \frac{[HCO_3^-]^2}{[CO_3^{2-}]}$$

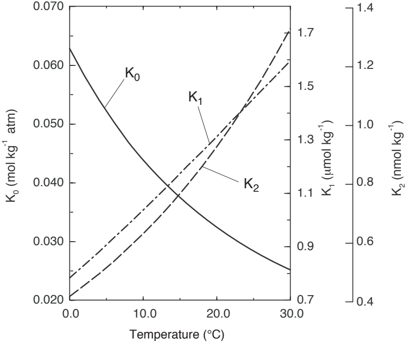
If we approximate *Alk* as

$$Alk \approx [HCO_3^-] + 2[CO_3^{2-}]$$

then we can write

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

Empirical equilibrium constants



Sarmiento & Gruber 2006

For instance:

$$\ln K_0 = 9345.17/T - 60.2409 + 23.3585 \ln(T/100) + S\left[0.023517 - 0.00023656\,T + 0.0047036(T/100)^2\right]$$

Weiss (1974)

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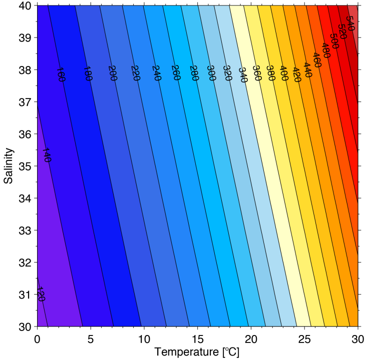
Variation of pCO_2 with S and T

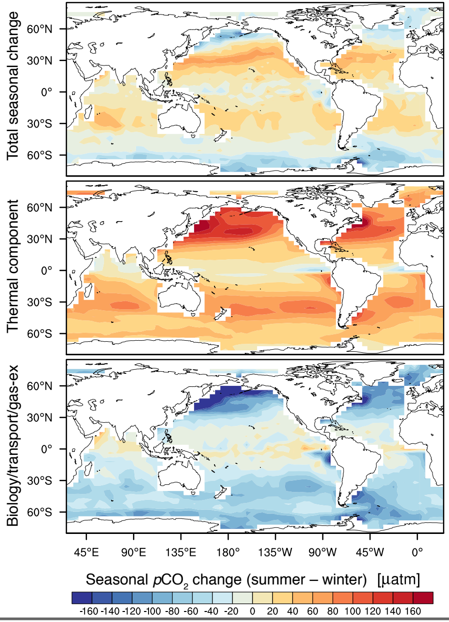


For *Alk* and *DIC* constant:

$$\frac{1}{pCO_2} \frac{\partial pCO_2}{\partial T} \approx 0.0423^\circ C$$

$$\frac{S}{pCO_2} \frac{\partial pCO_2}{\partial S} \approx 1$$

Seasonal Variability in pCO_2^{ocn}: thermal & biological effects



Seasonal amplitude of comparable magnitude to spatial variability in annual mean.

Mechanisms:

→ ΔSST

→ Biology (ΔDIC, ΔAlk)

\+ advection & gas exchange

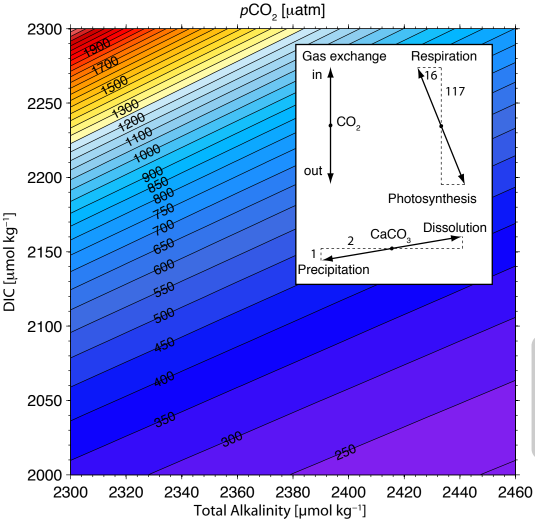
Thermal effect computed using:

$$\Delta pCO_2 = pCO_2^{win} \exp[0.0433(T^{sum} - T^{win}) - 4.35 \times 10^{-5}((T^{sum})^2 - (T^{win})^2)]$$

Summer = JFM (south) and JAS (north)

Winter = JAS (south) and JFM (north)

Inorganic carbon chemistry



Organic matter production

$$106\,CO_2 + 16\,NO_3^- + HPO_4^{2-} + 78\,H_2O + 18\,H^+ \rightleftharpoons C_{106}H_{175}O_{42}N_{16}P + 150\,O_2$$

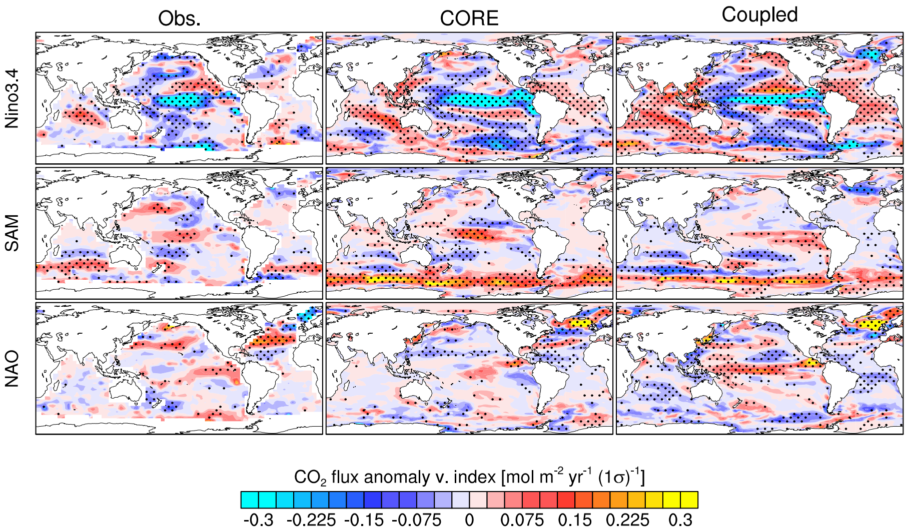
Formation/dissolution of $CaCO_3$

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3$$

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

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

Modeled air-sea CO_2 flux components



Discerning mechanisms governing variability in air-sea CO_2 flux

Monthly anomalies

$$Y' = Y - \overline{Y}_{mon}$$

Taylor series approximation

$$Y' \approx \sum_i \frac{\partial Y}{\partial X} X_i' + \mathcal{O}(X_i'^2, X_i' X_j')$$

Application to carbon system variables

$$J_{co_2}' \approx (k\gamma)'\overline{\Delta p\mathrm{CO}_2} + \overline{(k\gamma)}\Delta p\mathrm{CO}_2' + \left((k\gamma)'\Delta p\mathrm{CO}_2' - \overline{(k\gamma)'\Delta p\mathrm{CO}_2'}\right)$$

$$p\mathrm{CO}_2' \approx \frac{\partial p\mathrm{CO}_2}{\partial T}T' + \frac{\partial p\mathrm{CO}_2}{\partial S_{FW}}S' + \frac{\partial p\mathrm{CO}_2}{\partial DIC}sDIC' + \frac{\partial p\mathrm{CO}_2}{\partial Alk}sAlk'$$

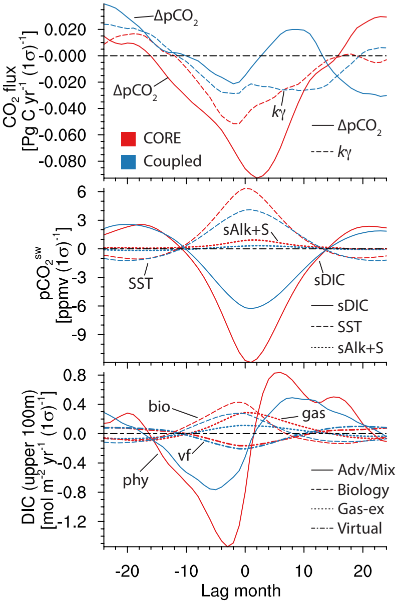
$$\int_0^{100} \left(\frac{\partial \mathrm{DIC}}{dt}\right)' dz = J_{co_2}' + J_{virtual}' + J_{bio}' + J_{phy}'$$

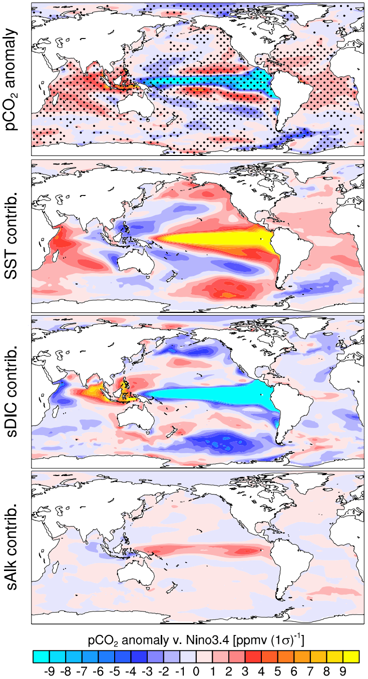
Climate variability

Regress Taylor-series components ($\frac{\partial Y}{\partial X} X_i'$) on climate indices ($\Psi$):

$$\frac{\partial Y}{\partial X} X_i' = \beta\Psi$$

Air-sea flux response to ENSO

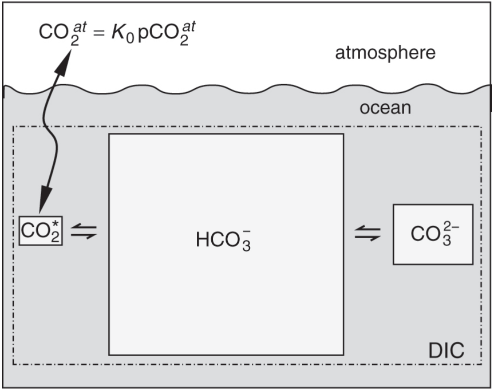




CO_2 uptake

How does *DIC* respond to gas exchange?

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



Williams and Follows, 2011

Assuming equilibrium, we know

$$[H_2CO_3^*] = K_0 pCO_2^{atm}$$

We can recast the carbonate equilibria as a buffering reaction

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

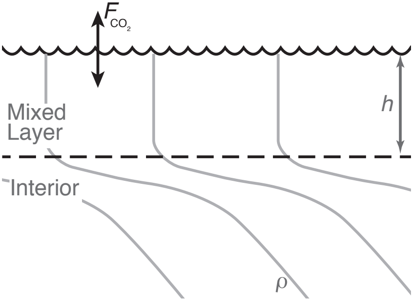
Gas exchange timescale for CO_2

No lateral exchange;
fluxes at $z = -h$ are zero:

$$\frac{\partial [A]}{\partial t} = \frac{k_w}{h}([A]_{eq} - [A])$$

if $[A]_{eq}$ = constant, then this is a first-order equation, with a characteristic timescale

$$\tau_{\text{gas-ex}} = h/k_w$$



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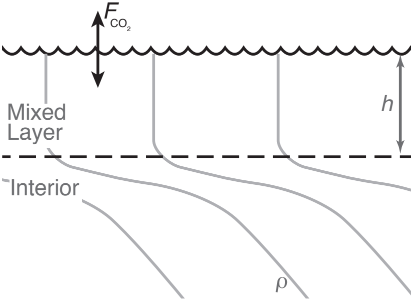

However, for CO_2, the entire *DIC* pool must equilibrate, thus we have

$$\frac{\partial DIC}{\partial t} = \frac{\partial DIC}{\partial [H_2CO_3^*]} \frac{\partial [H_2CO_3^*]}{\partial t} = \frac{k_w}{h}([H_2CO_3^*]_{eq} - [H_2CO_3^*])$$

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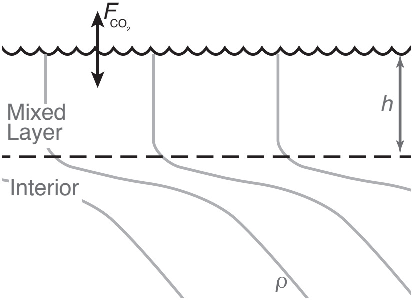

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Solving for $\partial[H_2CO_3^*]/\partial t$, we find

$$\frac{\partial [H_2CO_3^*]}{\partial t} = \left(\frac{\partial DIC}{\partial [H_2CO_3^*]}\right)^{-1}\frac{k_w}{h}([H_2CO_3^*]_{eq} - [H_2CO_3^*])$$

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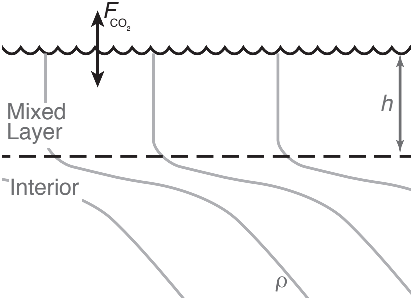

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So

$$\tau_{\text{gas-ex}} = \frac{\partial DIC}{\partial [H_2CO_3^*]}\left(\frac{h}{k_w}\right) \approx 20\left(\frac{h}{k_w}\right)$$

The Revelle Factor

Quantifying buffer capacity

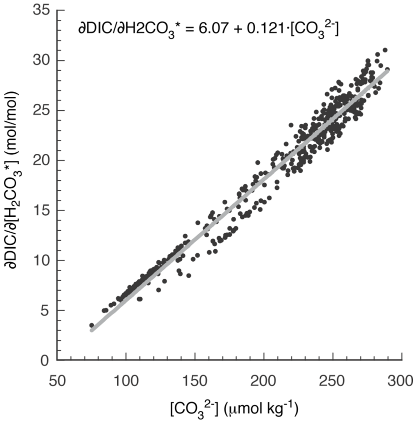
$$\frac{\partial DIC}{\partial[H_2CO_3^*]} = \frac{\partial DIC}{\partial(K_0 \cdot pCO_2)}$$
$$= \frac{\overline{DIC}}{\overline{pCO_2} \cdot K_0} \left(\frac{pCO_2}{DIC} \frac{\partial DIC}{\partial pCO_2} \right)$$
$$= \frac{\alpha}{K_0} \frac{1}{\gamma_{DIC}}$$

where

$$\gamma_{DIC} = \frac{DIC}{pCO_2} \frac{\partial pCO_2}{\partial DIC} \quad \text{and} \quad \alpha = \frac{\overline{DIC}}{\overline{pCO_2}}$$

γ_{DIC} is known as the 'Revelle Factor' or 'buffer factor'.

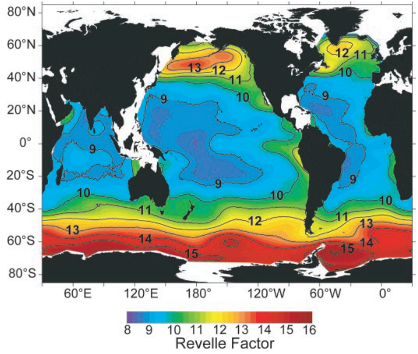
$$\tau_{\text{gas-ex}} = \frac{\partial DIC}{\partial[H_2CO_3^*]} \left(\frac{h}{k_w} \right)$$



Sarmiento and Gruber 2006

The Revelle Factor

Revelle Factor



$$\gamma_{DIC} = \frac{DIC}{pCO_2} \frac{\partial pCO_2}{\partial DIC}$$

Sabine et al. 2004

Ocean atmosphere partitioning

A pulse in atmospheric CO_2

$$\delta N^{atm} = \delta \chi_{CO_2} N^{atm}_{tot}$$

The increase in ocean carbon

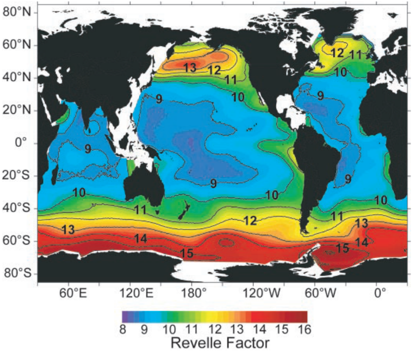
$$\delta N^{ocn} = \delta DIC \cdot m^{ocn}$$

Assume that pCO_2^{ocn} tracks pCO_2^{atm}

$$\delta pCO_2^{ocn} = \delta pCO_2^{atm} = \delta \chi_{CO_2} P^{atm}$$

The Revelle Factor

Revelle Factor



$$\gamma_{DIC} = \frac{DIC}{pCO_2}\frac{\partial pCO_2}{\partial DIC}$$

Sabine et al. 2004

Ocean atmosphere partitioning

A pulse in atmospheric CO_2

$$\delta N^{atm} = \delta\chi_{CO_2} N^{atm}_{tot}$$

The increase in ocean carbon

$$\delta N^{ocn} = \delta DIC \cdot m^{ocn}$$

Assume that pCO_2^{ocn} tracks pCO_2^{atm}

$$\delta pCO_2^{ocn} = \delta pCO_2^{atm} = \delta\chi_{CO_2} P^{atm}$$

We can use the Revelle Factor to estimate δDIC

$$\delta DIC = \delta pCO_2^{ocn} \cdot \frac{1}{\gamma_{DIC}} \cdot \frac{\overline{DIC}}{\overline{pCO_2^{ocn}}} = \delta pCO_2^{ocn} \cdot \frac{\alpha}{\gamma_{DIC}}$$

The ratio between the change in ocean and atmosphere inventories

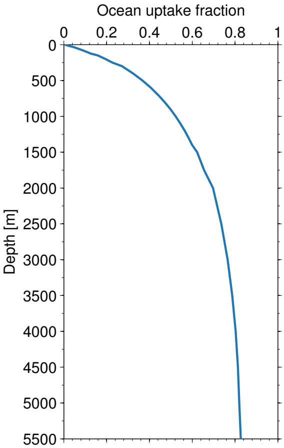
$$\frac{\delta N^{atm}}{\delta N^{ocn}} = \frac{\gamma_{DIC}}{\alpha}\frac{N^{atm}_{tot}}{P^{atm} m^{ocn}}$$

The ocean fraction

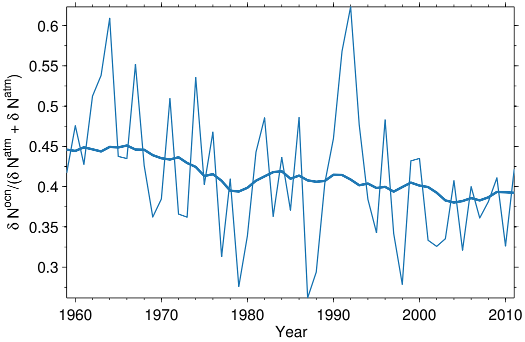
$$\frac{\delta N^{ocn}}{\delta N^{ocn} + \delta N^{atm}} = \left(\frac{\gamma_{DIC}}{\alpha}\frac{N^{atm}_{tot}}{P^{atm} m^{ocn}} + 1\right)^{-1}$$

CO_2 uptake

Ocean uptake fraction v. penetration depth



Global carbon budget

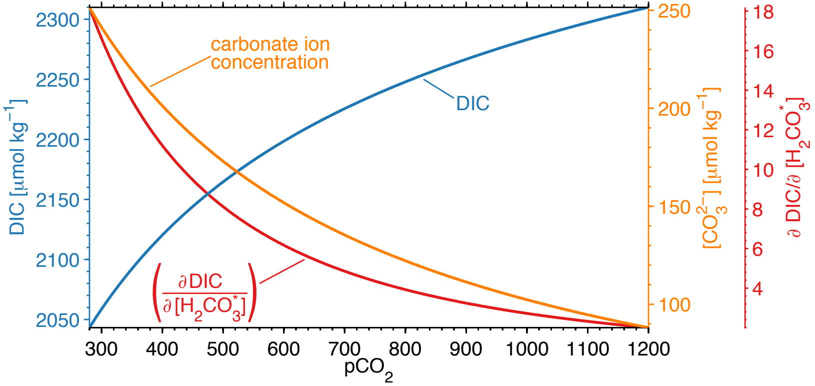


www.globalcarbonproject.org

CO_2 uptake

Equilibration to rising pCO_2^{atm}

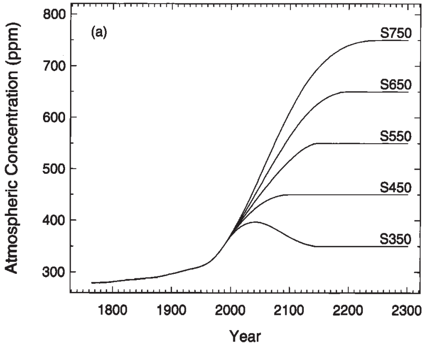
$$H_2CO_3^* + CO_3^{2-} \rightleftharpoons 2HCO_3^-$$

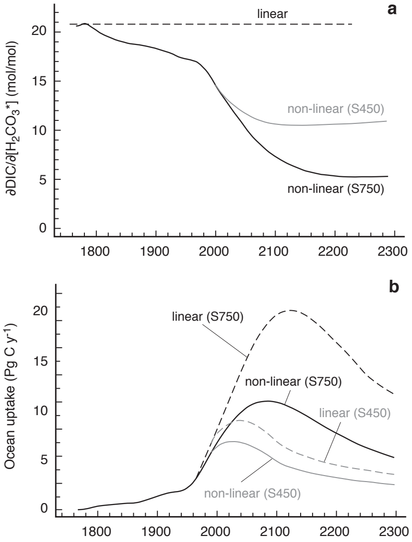


$T = 20^\circ$C; $S = 35$; $Alk = 2400\ \mu$eq kg^{-1}

CO_2 uptake

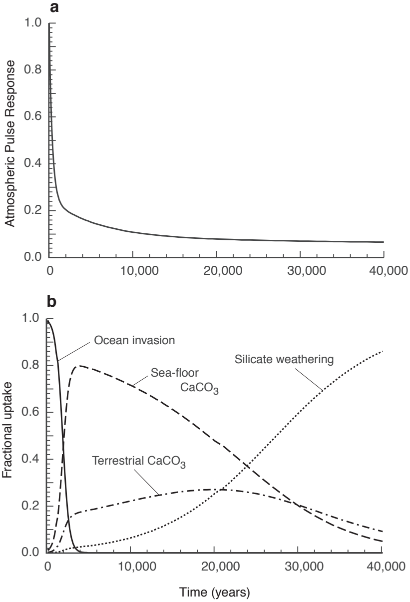
Carbon-carbon feedback





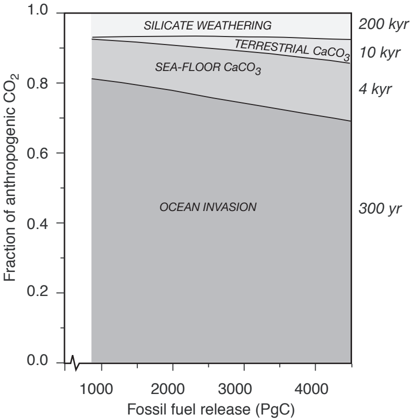
Sarmiento et al. 1995

The ultimate fate of anthropogenic CO_2



Sarmiento and Gruber 2006

(based on Archer et al. 1997)



Silicate weathering

$$2\,CO_2 + CaSiO_3 + 3\,H_2O \rightleftharpoons 2\,HCO_3^- + Ca^{2+} + Si(OH)_4$$

Summary

Main points

1. Gas exchange parameterizations are based on a loose application of an underlying conceptual model.

2. Wind speed is a dominant driver of the gas exchange velocity; a variety of methods have been used to develop empirical estimates of of the gas exchange velocity.

3. Carbon in seawater is distributed among *DIC* species according to acid-base equilibria; the system can be solved using empirically-derived equilibrium coefficients.

4. Ocean uptake of CO_2 is governed by reaction with carbonate ion; nonlinear chemistry results in diminished uptake with increasing pCO_2^{atm} as buffer capacity is consumed; the buffer capacity can be quantified by the Revelle Factor.