The CO_2 System in Seawater

General Introduction:

$pH = -\log([H^+]) \rightarrow pH = 8.1 \triangleq [H^+] = 10^{-8.1}$ µmol kg^{-1} or mmol m^{-3}, $pK_1 = -\log(K_1) \rightarrow pK_1 = 5.88 \triangleq K_1 = 10^{-5.88}$

Unknowns:

$CO_{2(gas)}$, $H_2CO_3^*$, HCO_3^-, CO_3^{2-}, H^+, OH^-, $B(OH)_4^-$, H_3BO_3, DIC, Alk

Reactions:

$$CO_{2(gas)} + H_2O \overset{K_0}{\leftrightarrow} H_2CO_3^* \left(i.\,e.\,CO_{2(aq)} + H_2CO_3\right) \quad (1)$$

$$H_2CO_3^* \overset{K_1}{\leftrightarrow} H^+ + HCO_3^- \quad (2)$$

$$HCO_3^- \overset{K_2}{\leftrightarrow} H^+ + CO_3^{2-} \quad (3)$$

$$H_2O \overset{K_w}{\leftrightarrow} H^+ + OH^- \quad (4)$$

$$H_3BO_3 + H_2O \overset{K_B}{\leftrightarrow} H^+ + B(OH)_4^- \quad (5)$$
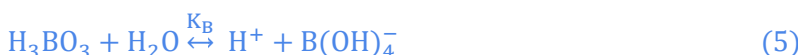
Equilibrium constants [careful: varying units]:

$$K_0 = \frac{[H_2CO_3^*]}{pCO_2} \quad (6)$$

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]} \quad (7)$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad (8)$$

$$K_w = [H^+][OH^-] \quad (9)$$

$$K_B = \frac{[H^+][B(OH)_4^-]}{[H_3BO_3]} \quad (10)$$

Concentration definitions [µmol kg^{-1} or mmol m^{-3}]:

$$DIC = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \quad (11)$$
$$\;\; 0.5\% \qquad 88.65\% \quad 10.9\%$$

$$Alk = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] + [B(OH)_4^-] \quad (12)$$
$$\;76.8\% \qquad 18.8\% \qquad\quad 0.2\% \qquad\quad 4.2\%$$

$$TB = [B(OH)_4^-] + [H_3BO_3] = c \cdot S \,\text{**} \quad (13)$$

** total boron concentration ∝ Salinity

combine (10) & (13) to $[B(OH)_4^-] = TB \cdot \left(\frac{[H^+]}{K_B} + 1\right)^{-1}$

Approximations:

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

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

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

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

Solution:

In models of the ocean carbon cycle, two cases are most commonly encountered: (a) specifying DIC and Alk and calculating pCO₂; (b) specifying pCO₂ and Alk and computing DIC.

(a) DIC and Alk

The goal is to rewrite the equation for Alk (12) in terms of the known parameters DIC and TB, and then solve the resulting equation for unknown $[H^+]$. As a first step, we use (7), (8), and the DIC definition (11) to write expressions for $[HCO_3^-]$ and $[CO_3^{2-}]$ that contain only $[H^+]$ as an unknown. In the case of $[HCO_3^-]$, this is done as follows. Solve (7) for $[H_2CO_3^*]$ and insert into the DIC definition. Similarly, solve (8) for $[CO_3^{2-}]$ and insert into the DIC definition. This gives

$$DIC = \frac{[H^+][HCO_3^-]}{K_1} + [HCO_3^-] + \frac{K_2[HCO_3^-]}{[H^+]} \quad (14)$$

Next, we use (8), solve it for $[HCO_3^-]$, and insert it into (14). This gives a second equation for DIC:

$$DIC = \frac{[H^+]^2[CO_3^{2-}]}{K_1 K_2} + \frac{[H^+][CO_3^{2-}]}{K_2} + [CO_3^{2-}] \quad (15)$$

Solving (14) for $[HCO_3^-]$ and (15) for $[CO_3^{2-}]$, respectively, and inserting the results into (12) eliminates $[CO_3^{2-}]$ and $[HCO_3^-]$ from this latter equation. The concentrations of $[OH^-]$ and $[B(OH)_4^-]$ are similarly eliminated using (9), (10), and (13). This results in our final equation, which is fourth order in the unknown $[H^+]$. This equation can then be solved for $[H^+]$ using an iterative approach. Once $[H^+]$ has been calculated, pCO₂ can be calculated from

$$pCO_2 = \frac{DIC}{K_0} \frac{[H^+]^2}{[H^+]^2 + K_1[H^+] + K_1 K_2} \leftrightarrow \frac{DIC}{K_0}\left(1 + \frac{[H^+]}{K_1} + \frac{[H^+]^2}{K_1 K_2}\right) \quad (16)$$

where this equation has been derived by solving (6) for pCO₂, and then using (7), (8), and (11) to eliminate the unknowns $[H_2CO_3^*]$, $[HCO_3^-]$ and $[CO_3^{2-}]$. See also (17) – (19) below.

(b) Alk and pCO_2:

Rewrite the equations for the three carbon species, i.e. (6), (7), and (8), in terms of $[H^+]$ and pCO_2, thus

$$[H_2CO_3^*] = K_0 pCO_2 \tag{17}$$

$$[HCO_3^-] = \frac{K_0 K_1 pCO_2}{[H^+]} \tag{18}$$

$$[CO_3^{2-}] = \frac{K_0 K_1 K_2 pCO_2}{[H^+]^2} \tag{19}$$

Substitute these terms into the equations for Alk (12) and also recast the other species, i.e., $[OH^-]$ and $[B(OH)_4^-]$, in terms of $[H^+]$ and total concentration. The resulting equation can again be solved using an iterative approach. Once $[H^+]$ is found, DIC is calculated using (11) and (17) – (19).

Simple answer to what controls surface pCO_2

$$pCO_2 = \frac{[H_2CO_3^*]}{K_0} = \frac{K_2}{K_0 \cdot K_1} \frac{[HCO_3^-]^2}{[CO_3^{2-}]} \approx \frac{K_2}{K_0 \cdot K_1} \frac{(2 \cdot DIC - Alk)^2}{Alk - DIC}$$

$\rightarrow pCO_2 = pCO_2(\text{physical \& biological processes})$
i) $K_2/(K_0 \cdot K_1)$ controlled by T & S
ii) DIC controlled by air-sea gas exchange & bio
iii) Alk only controlled by ocean biology

Summary of the most important pCO_2 sensitivities in seawater

Parameter	Definition	Mean Global	Mean High Latitudes	Mean Low Latitudes
Temperature	$\gamma_T = \dfrac{1}{pCO_2} \dfrac{\partial pCO_2}{\partial T}$	$0.0423°C^{-1}$	$0.0423°C^{-1}$	$0.0423°C^{-1}$
Salinity	$\gamma_S = \dfrac{S}{pCO_2} \dfrac{\partial pCO_2}{\partial S}$	1	1	1
DIC	$\gamma_{DIC} = \dfrac{DIC}{pCO_2} \dfrac{\partial pCO_2}{\partial DIC} = \dfrac{\partial \ln pCO_2}{\partial \ln DIC}$ *	10	13.3	9.5
Alk	$\gamma_{Alk} = \dfrac{Alk}{pCO_2} \dfrac{\partial pCO_2}{\partial Alk} = \dfrac{\partial \ln pCO_2}{\partial \ln Alk}$	–9.4	–12.6	–8.9
Freshwater	$\gamma_{freshwater} = \dfrac{S}{pCO_2} \dfrac{\partial pCO_2}{\partial S}$ $= \gamma_S + \gamma_{DIC} + \gamma_{Alk}$	1.6	1.7	1.6

* γ_{DIC} (Revelle factor) $\propto [CO_3^{2-}]^{-1} \propto \partial[H_2CO_3^*]/\partial DIC$
$\rightarrow$ measure of resistance to atmospheric CO_2 being absorbed by the surface ocean layers

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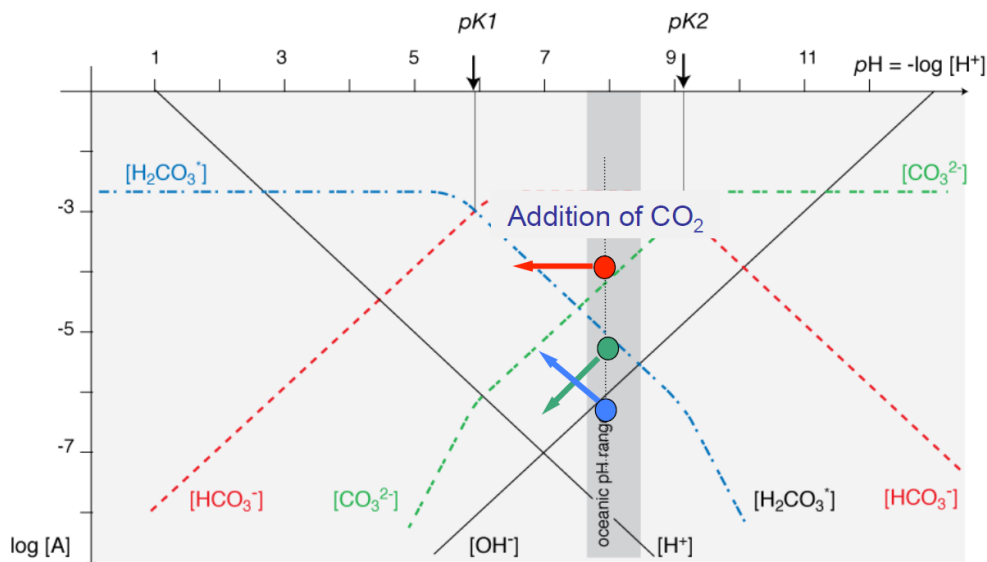
at oceanic pH = 8.1:
   $[H_2CO_3^*] : [HCO_3^-] : [CO_3^{2-}] \approx 0.5\% : 88.65\% : 10.9\%$
   $pCO_2 \approx 3.8 \cdot 10^2$ µatm

at pH = 5.5 (e.g. freshwater system):
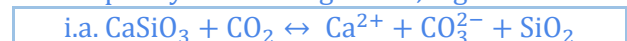 $[H_2CO_3^*] : [HCO_3^-] : [CO_3^{2-}] \approx 70\% : 30\% : 0.001\%$
   $pCO_2 \approx 3.33 \cdot 10^4$ µatm

ocean absorption to a good approximation:

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

river input by weathering of Ca–, Mg–Silicate:

$$\text{i.a. } CaSiO_3 + CO_2 \leftrightarrow Ca^{2+} + CO_3^{2-} + SiO_2$$

lysocline adjustment by $CaCO_3$ dissolution:

$$CaCO_3(s) \leftrightarrow Ca^{2+} + CO_3^{2-}$$

Take–Home Messages & Glacial–Interglacial Synthesis

Limitations to marine productivity: bottom up (a) & top down (b)
(a) temperature conditions
(a) light conditions
(a) availability of macronutrients (N, P, Si)
(a) availability of micronutrients (in part. Fe)
(b) zooplankton grazing

Limitations to terrestrial productivity:
- temperature conditions
- light conditions (most imp. at high lat.)
- water availability
- availability of nutrients (esp. N)
- CO_2 concentration

Estimating the land sink: bottom up (a) & top down (b)
(a) forest inventories: Φ estimate from measurements
(a) CO_2 flux co-variance: FLUXNET very sparse in tropics
(b) atm. CO_2 inversions: i.e. Mauna Loa sfc-atm. net C flux
- remote sensing: measure leaf area index, convenient
- modelling

Mechanisms for land sink:
- CO_2 fertilization: potentially large sink, esp. NH
- N fertilization: $\uparrow N_{ant.}$ = stimulates add. growth
- Past land-use change: fast CO_2 uptake at regrowth
- Climate change: $\uparrow$sink due to warming in high lat. & strong negative response in low lat. (drying)

Ocean carbon cycle feedbacks:
- ocean surface warming feedback $+$
$\downarrow$solubility $\rightarrow \downarrow CO_2$ uptake
- ocean biogeochemical-loop (circulation) feedback $-$
$\uparrow$stratification limits upward DIC & nutrients $\rightarrow \downarrow CO_{2,\,out}$
- ocean biogeochemical-loop (biota) feedback $-/+$
$\uparrow$stratification $\rightarrow \uparrow/\downarrow$productivity $\rightarrow \uparrow/\downarrow \Phi_{Corg}$ downward
- carbonate chemistry chemical feedback $+$
uptake $CO_2 \rightarrow \downarrow CO_3^{2-} \triangleq \uparrow \gamma_{DIC} \rightarrow$ limit capacity CO_2 uptake
- circulation feedback $+$
$\downarrow$AMOC $\rightarrow$ less transport of CO_2 into ocean interior
$+ \triangleq$ positive & $- \triangleq$ negative feedback

Land carbon cycle feedbacks:
- CO_2 fertilization feedback $-$
$\uparrow CO_2 \rightarrow \uparrow$plant H_2O-use efficiency $\rightarrow \uparrow CO_2$ uptake
- climate feedback for land vegetation $-/+$
$\uparrow CO_2$ may $\rightarrow \uparrow$T & R perturbations $\rightarrow \uparrow/\downarrow$growth of land vegetation $\triangleq \uparrow/\downarrow$land CO_2 uptake & ultimately f_{air}
- climate feedback for soil carbon $+$
$\uparrow$SH flux into soil may $\rightarrow \uparrow$decomposition (higher resp.) $\rightarrow \uparrow$soil carbon being lost to atm. $\triangleq \uparrow CO_2^{atm.}$
- other potential feedbacks include $-/+$
land cover/vegetation, $CH_2/N_2O/CO_2$ feedbacks, etc.

Upwelling on–/ offshore profile of CO_2 determined by:
1. circulation (upwelling)
2. solubility (temperature)
3. biology (photosynthesis & export)
4. gas exchange (δpCO_2)

Biological soft-tissue pump:
- efficiency $\triangleq$ measure of success of phytoplankton in maintaining low nutrient concentrations in the surface ocean
- strength $\triangleq$ magnitude of the downward flux of organic matter

Explaining the 100ppm CO_2 difference during G—IG: *

loss of C from bio (~500 PgC)	$+15$ µatm
colder SST ($\sim -4°C$)	-32 µatm
lower sea-level ($\uparrow S \triangleq \uparrow pCO_2$)	$+12$ µatm
sum	~ 0 µatm
target	-80 to -100 µatm

Physical & biological mechanisms to close the Southern Ocean window & reduce outgassing of CO_2:
1. by adding a physical barrier, i.e. sea-ice
2. by stratifying the SO or by reducing upwelling
3. by increasing export of organic matter

*** $CO_{2,foss.}[Pg\,C] = \dfrac{\text{mixing ratio [ppm]} \cdot 10^{-6} \cdot N_{atm.} \cdot M_C}{10^{15}}$
$\rightarrow 2.14$ Pg C $\triangleq 2.14 \cdot 10^{15}$ g C ≈ 1 ppm ≈ 1 µatm

Deglaciation sequence	Antarctica: $\downarrow$atm. $\Delta^{14}C \triangleq \uparrow$Dome C $CO_2 \triangleq \uparrow F(SIO_2 \cdot nH_2O) \triangleq \uparrow$ Feb. SST $\triangleq \uparrow$Dome C δD
Bipolar see-saw	$\downarrow \delta^{18}O$ (Greenland) $\triangleq \uparrow \delta^{18}O$ (Antarctica = Ant.) $\triangleq \uparrow CO_2^{atm.}$ (Ant.) $\triangleq \uparrow$Opal Flux (Ant.)
LGM to Holocene	$\uparrow CO_2^{atm.}$ at 18 ka $\triangleq \downarrow$Fe-flux (at ODP1090) $\triangleq \downarrow \delta^{15}N \triangleq \downarrow \Phi$Alkenones $\triangleq \downarrow$Fe-flux (at EDC, Ant.)

Carb. comp.
- $CO_2^{atm.}$ input of 500 Pg C $\rightarrow$ acidifies ocean, $\downarrow[CO_3^{2-}] \rightarrow$ shoaling of saturation horizon & dissolution of $CaCO_3$ supplies CO_3^{2-} again to balance Alk out
- with lysocline shoaled, positive imbalance exists between riverine input of Alk & net removal of Alk by $CaCO_3$ burial $\rightarrow \uparrow[CO_3^{2-}]$ decreases the oceanic buffer factor (γ_{DIC}) which permits the ocean to absorb add. CO_2 from the atm. $\rightarrow \downarrow$saturation horizon as Alk is removed by $CaCO_3$ burial

Southern Ocean Synthesis Framework

- cooler conditions during LGM → northward **shift of westerlies** & ↓upwelling of deep water in the Antarctic
- cold but fresh stable surface layer with frequent **substantial ice coverage** further ↓CDW ventilation
- response: **decreased bioproductivity** and **enhanced stratification** in **Antarctic** but utilization of NO_3^- goes up indicating drop in upward supply larger than ↓biological export
- higher dust input from the atm. is not large enough to overcome the physically-induced reduction in phytoplankton production in the Antarctic
- however, dust is large enough to alleviate diatoms from Fe stress → lower SI utilization in this region

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- glacial **sub-Antarctic** is **more productive**, perhaps due to shifted westerlies & increased supply of iron
- sub-Antarctic utilization of nitrate & phosphate does not change much → why: increased nutrient supply from the thermocline offsets effect of observed ↑productivity
- changes suggest a combined **physically** & **biologically induced** closure of the SO window reducing atm. CO_2

- changes in the SO linked with changes throughout the rest of the ocean
- possibly due to dust, degree of NO_3^- utilization higher in both regions → ↓surface nitrate & less nutrient transport to lower latitudes and which causes the O_2 minimum zone to migrate into the abyssal ocean & reduced release of CO_2 from the SO
- higher dust flux to glacial SO also lowers Si-to-NO_3^- uptake ratio of diatoms there, leading to lower $Si(OH)_4$ utilization (leaking the Southern Ocean Si trap) by providing Si to the low latitudes
- this causes a phytoplankton community shift from coccolithophorids to diatoms
- the resulting lowered export of $CaCO_3$ relative to C_{org} then reduces atm. CO_2 through **CaCO₃ compensation**

Modern ocean and Southern Ocean-based synthesis