Climate Dynamics (6)
The biogeochemistry of CO_2 and Climate

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CO_2 as a biogeochemical

- ♦ CO_2 (i.e. Σ CO_2 = DIC) is a non-limiting plant nutrient, utilised in photosynthesis (~10%)
  - N.B. DIC = CO_2(aqu) + bicarbonate + carbonate
- ♦ In the ocean, the stoichiometry (P:N:C:O) is defined by the **Redfield ratios**
- ♦ CO_2 in the atmosphere (partial pressure, i.e. pCO_2) is in long-term equilibrium with CO_2 in the ocean
  - but N.B. unsteady in short term : there is a strong seasonal cycle (in anti-phase between N & S hemispheres)
- ♦ How does CO_2 draw-down by biological production in the ocean affect atmospheric CO_2 ?

Factors affecting CO_2 speciation

- Biological production and respiration
- Acidity (pH, hydrogen ion concentration)
- $CaCO_3$ precipitation and dissolution
  - Solubility product SP= $[Ca] \times [CO_3]$
- Balance/imbalance between DIC and Alkalinity
- N.B. Residence time of Ca (w.r.t. river input & carbonate deposition) is ~ 1 Myr
- but precipitation and dissolution (modified by circulation and mixing) cause local variations of [Ca] of the order of 1%, i.e. 200 uM/kg
  - causes variation of alkalinity (~ analogous to salinity)

Basic chemistry of CO_2 and water

$$
\begin{array}{lll}
CO_2 + H_2O & \text{gaseous} & \\
\quad \updownarrow \quad \text{[Henry's Law]} & & \\
H_2CO_3 & \text{carbonic acid} & \text{(acid)} \\
\quad \updownarrow & & \\
H^+ + HCO_3^- & \text{bicarbonate} & \text{(neutral)} \\
\quad \updownarrow & & \\
2H^+ + CO_3^{2-} & \text{carbonate} & \text{(alkaline)}
\end{array}
$$

Alkalinity

Alkalinity = $\sum$ strong positive ions - $\sum$ strong negative ions

= - Acidity {which is not much used, and not the same as pH, or even $[H^+]$ }

N.B. weak ions (including H^+ and OH^-) are excluded...

e.g. 0.1 M solurion of NaOH in water $\Rightarrow$ Alk = $[Na^+]$ = +0.1 M

e.g. 0.1 M solurion of HCl in water $\Rightarrow$ Alk = -$[Cl^-]$ = - 0.1 M {Acidity = 0.1 M, pH = 1.0}

e.g. 0.1 M solurion of NaCl in water $\Rightarrow$ Alk = $[Na^+]$ - $[Cl^-]$ = 0 {neutral}

N.B. "strong positive ions" includes Ca^{2+}, which is variable and the main determinant of alkalinity in seawater

But since charge balance requires...

$\sum$ strong positive ions + $\sum$ weak positive ions - $\sum$ strong negative ions - $\sum$ weak negative ions = 0

Alkalinity = $\sum$ weak negative ions - $\sum$ weak positive ions

= $[OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H^+]$ etc...

This sum of weak ionic concentrations is therefore fixed (set) by $[Na^+] + [K^+] + 2[Ca^{2+}] - [Cl^-] - 2[So_4^{2-}]$....

Alkalinity and Total CO_2

in practice the important ions are usually H^+, OH^-, HCO_3^-, and CO_3^{2-}

$\therefore$ Alkalinity = $[OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H^+]$

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

$\approx$ 2400 ì M/kg

Total CO2 = $\sum$ CO2 = DIC = $[H_2CO_3]$ + $[HCO_3^-]$ + $[CO_3^{2-}]$

1% 95% 4%

$\approx$ 2300 ì M/kg

Practical Carbonate System Calculations

Any two CO_2 system quantities are sufficient to determine all the others
Alk and DIC are usually measured, and so are used most commonly
{ pCO_2, pH, and $[CO_3^{2-}]$ are usually derived from them }

for example...

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

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

$\therefore [CO_3^{2-}] \approx Alk - DIC \approx 2400 - 2300 \approx 100$ ì M/kg

and so, also, $[HCO_3^-] \approx 2\,DIC - Alk \approx 2200$ ì M/kg

Moreover, since $H_2O + CO_2 + CO_3^{2-} \leftrightarrow 2\,HCO_3^-$, {const = K}

$pCO2 = [CO2]/$á $= [HCO3^-]^2/$á $K[CO_3^{2-}]$

Calcium Carbonate formation at low CO_2 level (alkaline, high pH)

from rocks | from volcanoes

$CaO + 2H_2O + CO_2$

$\updownarrow$

$Ca(OH)_2 + H_2CO_3$

$\updownarrow$

$Ca^{++} + HCO3^- + OH^- + H_2O$

$\updownarrow$

$Ca^{++} + CO3^{2-} + 2H_2O$

$\updownarrow$

$CaCO_3 + 2H_2O$

to sediments

Calcium Carbonate dissolution at high CO_2 level (acidic, low pH)

from rocks | from volcanoes

$CaO + 3H_2O + 2CO_2$

$\updownarrow$

$Ca(OH)_2 + 2\,H_2CO_3$

$\updownarrow$

$Ca^{++} + 2\,HCO3^- + 2H_2O$

$\updownarrow$

$CaCO_3 + HCO3^- + H^+ + 2H_2O$

$\updownarrow$

$CaCO_3 + H_2CO3 + 2H_2O$

$\updownarrow$

$CaCO_3 + 3H_2O + CO_2$

Calcium Carbonate & the CO_2 system

- ♦ Calcite/aragonite precipation (by plankton)
  - decreases DIC by 1 unit, alkalinity by 2 units
  - on average (!) plankton use 1 Ca per 3 C atoms
  - (coccolithophores & forams, but not diatoms !)
- ♦ Calcite/aragonite dissolution (essentially inorganic, but accelerated by bacterial respiration creating acidic micro-environments ?)
  - vice versa, i.e. +1 DIC : +2 Alk
  - occurs (partially) below lysocline
  - fully below CCD (calcite compensation depth)
- ♦ N.B. solubility product of $CaCO_3$ increases markedly with pressure (and therefore depth)

Overall effects

- ♦ Primary production (in surface waters)
  - decreases DIC by ~ 200 uM/kg and alkalinity by ~ 150 uM/kg
  - and thus decreases pCO_2 (from 1000 ppm to 250 ppm)
- ♦ Respiration (in sub-surface waters)
  - increases DIC (but not alkalinity)
  - causing large increase in pCO_2 (and decrease of pH)
- ♦ Calcite dissolution (in deep waters only)
  - increases both DIC and alkalinity
  - causing small decrease in pCO_2 (and increase of pH)
- ♦ Doubling primary production (e.g. by increased upwelling of nutrients) could halve surface pCO_2 (to ca 150 ppm)

Other interesting issues

- ♦ Possible feedback on temperature
- ♦ Effects of altered primary production during glaciations (and/or atmospheric CO_2 from volcanoes) on lysocline depths (etc)
  - NB there are longer term effects too, because of altered burial of carbonates (affects both DIC and Ca conc'ns)
- ♦ Effects of CO_2 injection (sequestration) in deep water
  - will increase carbonate dissolution and decrease burial...