

Climate Dynamics (6)

The biogeochemistry of CO₂ and Climate

John Shepherd

School of Ocean & Earth Science
Southampton Oceanography Centre
University of Southampton

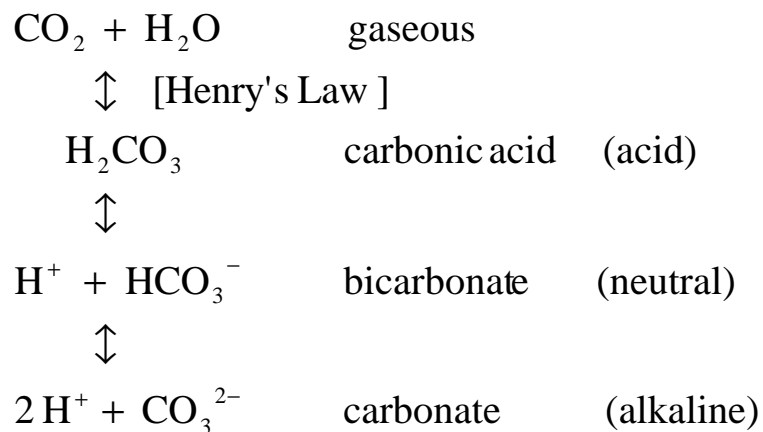
CO₂ as a biogeochemical

- ◆ CO₂ (i.e. $\Sigma \text{CO}_2 = \text{DIC}$) is a non-limiting plant nutrient, utilised in photosynthesis (~10%)
 - N.B. $\text{DIC} = \text{CO}_2(\text{aqu}) + \text{bicarbonate} + \text{carbonate}$
- ◆ In the ocean, the stoichiometry (P:N:C:O) is defined by the **Redfield ratios**
- ◆ CO₂ in the atmosphere (partial pressure, i.e. pCO₂) is in long-term equilibrium with CO₂ 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 CO₂ draw-down by biological production in the ocean affect atmospheric CO₂ ?

Factors affecting CO₂ speciation

- ◆ Biological production and respiration
- ◆ Acidity (pH, hydrogen ion concentration)
- ◆ CaCO₃ 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 CO₂ and water



Alkalinity

$$\text{Alkalinity} = \sum \text{strong positive ions} - \sum \text{strong negative ions}$$

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

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

e.g. 0.1M solution of NaOH in water $\Rightarrow \text{Alk} = [\text{Na}^+] = +0.1 \text{ M}$

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

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

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

$$\text{Alkalinity} = \sum \text{weak negative ions} - \sum \text{weak positive ions}$$

$$= [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] - [\text{H}^+] \text{ etc...}$$

This sum of weak ionic concentrations is therefore fixed (set) by $[\text{Na}^+] + [\text{K}^+] + 2[\text{Ca}^{2+}] - [\text{Cl}^-] - 2[\text{SO}_4^{2-}] \dots$

Alkalinity and Total CO_2

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

$$\therefore \text{Alkalinity} = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] - [\text{H}^+]$$

$$\approx [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$$

$$\approx 2400 \text{ } \mu\text{M/kg}$$

$$\text{Total CO}_2 = \sum \text{CO}_2 = \text{DIC} = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

$$\begin{array}{ccc} 1\% & 95\% & 4\% \end{array}$$

$$\approx 2300 \text{ } \mu\text{M/kg}$$

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 $[\text{CO}_3^{2-}]$ are usually derived from them }

for example...

$$\text{Alk} \approx [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$$

$$\text{DIC} \approx [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

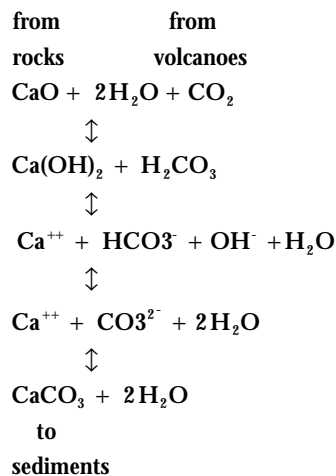
$$\therefore [\text{CO}_3^{2-}] \approx \text{Alk} - \text{DIC} \approx 2400 - 2300 \approx 100 \text{ } \mu\text{M/kg}$$

$$\text{and so, also, } [\text{HCO}_3^-] \approx 2 \text{ DIC} - \text{Alk} \approx 2200 \text{ } \mu\text{M/kg}$$

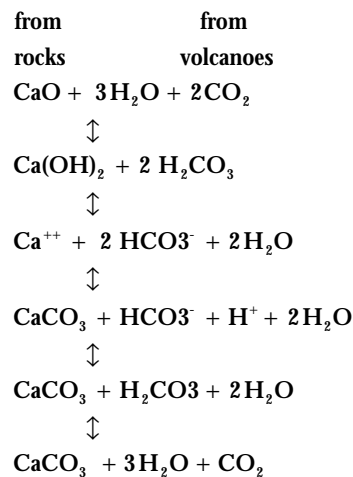
Moreover, since $\text{H}_2\text{O} + \text{CO}_2 + \text{CO}_3^{2-} \leftrightarrow 2\text{HCO}_3^-$, {const = K}

$$\text{pCO}_2 = [\text{CO}_2] / a = [\text{HCO}_3^-]^2 / a K [\text{CO}_3^{2-}]$$

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



Calcium Carbonate dissolution at high CO₂ level (acidic, low pH)



Calcium Carbonate & the CO₂ system

- ◆ Calcite/aragonite precipitation (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 CaCO₃ 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 pCO₂ (from 1000 ppm to 250 ppm)
- ◆ Respiration (in sub-surface waters)
 - increases DIC (but not alkalinity)
 - causing large increase in pCO₂ (and decrease of pH)
- ◆ Calcite dissolution (in deep waters only)
 - increases both DIC and alkalinity
 - causing small decrease in pCO₂ (and increase of pH)
- ◆ Doubling primary production (e.g. by increased upwelling of nutrients) could halve surface pCO₂ (to ca 150 ppm)

Other interesting issues

- ◆ Possible feedback on temperature
- ◆ Effects of altered primary production during glaciations (and/or atmospheric CO₂ 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 CO₂ injection (sequestration) in deep water
 - will increase carbonate dissolution and decrease burial...