

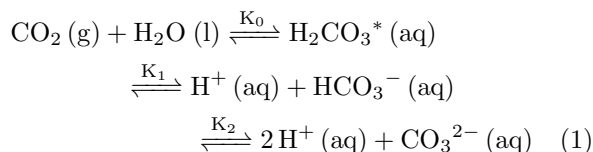
Carbonate Chemistry and pCO₂

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The atmospheric concentration of carbon dioxide (pCO₂) is a primary factor influencing global climate today and through deep time. The oceanic inorganic carbon reservoir is over 50 times that of the atmosphere, so atmosphere-ocean exchange drives pCO₂ over millennial timescales. The goal of this section is to derive a quantitative model which relates pCO₂ to the measurable ocean carbonate system.

When CO₂ dissolves, it reacts with water to form carbonic acid (H₂CO₃^{*})¹, bicarbonate (HCO₃⁻), and carbonate (CO₃²⁻). These reactions are reversible, so the following equilibrium is established:



K_{0,1,2} are measurable concentration ratios of reactants by products at equilibrium:

$$K_0 = [\text{H}_2\text{CO}_3^*]/\text{pCO}_2 \quad (2)$$

$$K_1 = [\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3^*] \quad (3)$$

$$K_2 = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-] \quad (4)$$

Dissolved Inorganic Carbon (DIC) and Alkalinity (Alk) are also measurable:

$$\begin{aligned} \text{DIC} &= [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \\ &\approx [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \end{aligned} \quad (5)$$

Alk is the charge-balanced² excess of bases in solution, primarily carbonic conjugate bases:

$$\begin{aligned} \text{Alk} &= [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + \\ &\quad [\text{B}(\text{OH})_4^-] + (\Sigma[\text{B}] - \Sigma[\text{A}]) \\ &\approx [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \end{aligned} \quad (6)$$

Rearranging equilibrium constant expressions gives:

$$[\text{H}^+] = K_2 \cdot [\text{HCO}_3^-]/[\text{CO}_3^{2-}] \quad (4)$$

$$[\text{H}_2\text{CO}_3^*] = [\text{H}^+][\text{HCO}_3^-]/K_1 \quad (3)$$

$$\text{pCO}_2 = [\text{H}_2\text{CO}_3^*]/K_0 \quad (2)$$

Sequential substitution and simplification gives:

$$\text{pCO}_2 = \frac{K_2}{K_0 \cdot K_1} \cdot \frac{[\text{HCO}_3^-]^2}{[\text{CO}_3^{2-}]} \quad (7)$$

Subtracting (6) from (5) and substituting the result back into (5) gives:

$$[\text{CO}_3^{2-}] \approx \text{Alk} - \text{DIC} \quad (8)$$

$$[\text{HCO}_3^{2-}] \approx 2\text{DIC} - \text{Alk} \quad (9)$$

Finally, substituting back into (7) gives:

$$\text{pCO}_2 \approx \frac{K_2}{K_0 \cdot K_1} \cdot \frac{(2\text{DIC} - \text{Alk})^2}{\text{Alk} - \text{DIC}} \quad (10)$$

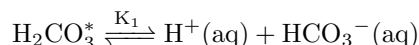
1 Calcium

The complexity of the carbonate system leads to some counter-intuitive dynamics. One of these is the

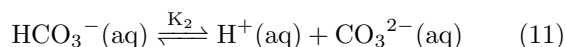
¹It is difficult to distinguish between dissolved carbon dioxide and carbonic acid, so they are grouped as a single species

²Concentrations of species which exchange more than one proton are scaled accordingly.

observation that an increase in $[\text{H}_2\text{CO}_3^*]$ has the effect of *lowering* $[\text{CO}_3^{2-}]$. To understand why, recall from (1):



By Le Chatelier's principle, increasing the concentration of the reactant H_2CO_3^* will shift the reaction to the right, and thus more H^+ and HCO_3^- will be produced in equal measure, say by amount a . Next, consider how this increase affects the balance of the next equilibrium (1):



Recall that the equilibrium concentrations of the products in this reaction are much lower than the product. Thus, the same increase $+a$ to both sides will have a greater effect on the products, shifting the equation to the left (converting CO_3^{2-} to HCO_3^-). With the addition of carbonic acid, carbonate alkalinity is consumed. Or, in terms of the equilibrium constant expression:

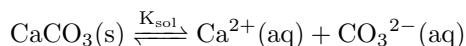
$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (4)$$

Solving for $[\text{CO}_3^{2-}]$:

$$[\text{CO}_3^{2-}] \propto \frac{[\text{HCO}_3^-]}{[\text{H}^+]} \gg 1$$

Clearly, as a increases with the addition of H_2CO_3^* , $[\text{CO}_3^{2-}]$ will decrease. The concentration of carbonate is of key concern in another geochemical system, the biological calcium carbonate pump.

Calcium carbonate forms two minerals, calcite and aragonite, which many ocean organisms use to build shells and exoskeletons.



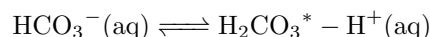
$$K_{\text{sol}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$$

$$\begin{aligned} [\text{Ca}^{2+}] &= 10 \text{ mmol kg}^{-1} \\ [\text{CO}_3^{2-}] &\approx 40 \text{ to } 200 \text{ } \mu\text{mol kg}^{-1} \end{aligned}$$

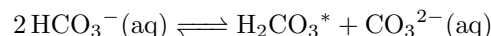
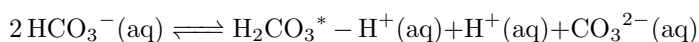
The saturation state of calcite or aragonite:

$$\Omega = \frac{[\text{CO}_3^{2-}]_{\text{meas.}}}{[\text{CO}_3^{2-}]_{\text{equil.}}} \quad (12)$$

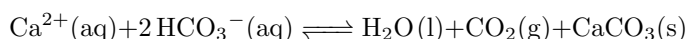
Rearranging equation 2.,



Adding equation 3.,



Interacting with calcium,



Thus, calcification consumes 2 units of DIC, releasing only 1 unit as a byproduct.