# Chapter 4

# $pCO_2$ & Marine Carbonate Derivation

The atmospheric concentration of carbon dioxide ($pCO_2$) 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 $pCO_2$ over millennial timescales. The goal of this section is to derive a quantitative model which relates $pCO_2$ to the measurable ocean carbonate system.

When $CO_2$ dissolves, it reacts with water to form carbonic acid ($H_2CO_3{}^*$)[1], bicarbonate ($HCO_3{}^-$), and carbonate ($CO_3{}^{2-}$). These reactions are reversible, so the following equilibrium is established:

$$\begin{aligned} \mathrm{CO_2\,(g) + H_2O\,(l)} &\xrightleftharpoons{\mathrm{K_0}} \mathrm{H_2CO_3{}^*\,(aq)} \\ &\xrightleftharpoons{\mathrm{K_1}} \mathrm{H^+\,(aq) + HCO_3{}^-\,(aq)} \\ &\xrightleftharpoons{\mathrm{K_2}} \mathrm{2\,H^+\,(aq) + CO_3{}^{2-}\,(aq)} \end{aligned} \tag{4.1}$$

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

$$\mathrm{K_0 = [H_2CO_3{}^*]/pCO_2} \tag{4.2}$$

$$\mathrm{K_1 = [H^+][HCO_3{}^-]/[H_2CO_3{}^*]} \tag{4.3}$$

$$\mathrm{K_2 = [H^+][CO_3{}^{2+}]/[HCO_3{}^-]} \tag{4.4}$$

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

$$\begin{aligned} \mathrm{DIC} &= \underset{0.5\%}{[\mathrm{H_2CO_3^*}]} + \underset{88.6\%}{[\mathrm{HCO_3^-}]} + \underset{10.9\%}{[\mathrm{CO_3^{2-}}]} \\ &\approx \mathrm{[HCO_3{}^-] + [CO_3{}^{2-}]} \end{aligned} \tag{4.5}$$

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

Alk is the charge-balanced[2] excess of bases in solution, primarily carbonic conjugate bases:

$$\begin{aligned} \mathrm{Alk} &= \underset{76.8\%}{[\mathrm{HCO_3^-}]} + 2\underset{18.7\%}{[\mathrm{CO_3^{2-}}]} + \\ &\quad \underset{4.2\%}{[\mathrm{B(OH)_4^-}]} + \underset{0.2\%}{(\Sigma[\mathrm{B}] - \Sigma[\mathrm{A}])} \\ &\approx \mathrm{[HCO_3{}^-] + 2\,[CO_3{}^{2-}]} \end{aligned} \tag{4.6}$$

Rearranging equilibrium constant expressions gives:

$$\mathrm{[H^+] = K_2 \cdot [HCO_3{}^-]/[CO_3{}^{2-}]} \tag{4.4}$$

$$\mathrm{[H_2CO_3{}^*] = [H^+][HCO_3{}^-]/K_1} \tag{4.3}$$

$$\mathrm{pCO_2 = [H_2CO_3{}^*]/K_0} \tag{4.2}$$

Sequential substitution and simplification gives:

$$\mathrm{pCO_2} = \frac{\mathrm{K_2}}{\mathrm{K_0 \cdot K_1}} \cdot \frac{\mathrm{[HCO_3{}^-]^2}}{\mathrm{[CO_3{}^{2-}]}} \tag{4.7}$$

Subtracting (4.6) from (4.5) and substituting the result back into (4.5) gives:

$$\begin{aligned} \mathrm{[CO_3{}^{2-}]} &\approx \mathrm{Alk - DIC} \\ \mathrm{[HCO_3{}^{2-}]} &\approx \mathrm{2DIC - Alk} \end{aligned}$$

Finally, substituting back into (4.7) gives:

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

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