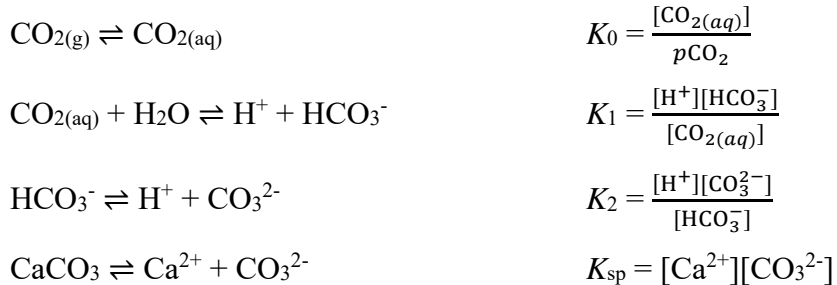


On the relationship between CO₂ and CaCO₃

The purpose of this addendum is to clarify, as simply as possible, the relationship between CO₂ and CaCO₃ in an aqueous carbonate system. The relevant carbonate equilibria are shown below. In the ocean, there are other equilibria, too, which we are omitting here for clarity.



It is also useful to introduce $\sum\text{CO}_2$, the total amount of dissolved inorganic carbon in the system, and Alkalinity, the amount of H⁺ required to titrate DIC to neutrality:

$$\begin{aligned} \sum\text{CO}_2 &= [\text{CO}_{2(aq)}] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \\ \text{Alkalinity} &= [\text{HCO}_3^-] + 2 \times [\text{CO}_3^{2-}] \end{aligned}$$

These expressions do not depend directly on pH. Note that carbonate precipitation decreases $\sum\text{CO}_2$ by removing CO₃²⁻ from the system, whereas respiration of organic matter increases $\sum\text{CO}_2$ by adding CO_{2(aq)} to the system. Precipitation also decreases Alkalinity by 2 units for each unit of CO₃²⁻ removed from the system.

Respiration of organic matter increases [CO_{2(aq)}] and $\sum\text{CO}_2$. It will acidify the water, mainly through the equilibrium K_1 (Le Châtelier's principle says the reaction goes to the right), but also somewhat through K_2 as [HCO₃⁻] increases. Every unit increase in [CO₃²⁻] through the reshuffling of DIC species is accompanied by 2 units of [H⁺]. However, because both K_1 and K_2 contain [H⁺] terms, this reshuffling actually places K_2 out of mass balance. CO₃²⁻ cannot be sourced from DIC without also adding [H⁺]. Something else has to donate CO₃²⁻ in order to maintain equilibrium for K_2 . That something is CaCO₃, which dissolves to meet the "demand" for CO₃²⁻. We then arrive at a familiar idea, that the addition of CO_{2(aq)} results in CaCO₃ dissolution.

Consider, then, what happens when CaCO₃ precipitates. $\sum\text{CO}_2$ decreases when CO₃²⁻ is removed as CaCO₃, but H⁺ is not consumed in the process. As a result, there is an excess of H⁺. During the DIC reshuffling process, the only way to balance the DIC species is actually to "get rid" of some H⁺. For example, Le Châtelier's principle could push K_2 to the right (there is not enough CO₃²⁻), but that would exacerbate the [H⁺] problem. The only way to rebalance the DIC pool is to react H⁺ with HCO₃⁻. There is thus a further drop in $\sum\text{CO}_2$ through CO₂ release. Henry's law still applies, so the increase in [CO_{2(aq)}] from CaCO₃ precipitation also ends up increasing pCO₂.