On the relationship between CO_2 and $CaCO_3$

The purpose of this addendum is to clarify, as simply as possible, the relationship between CO_2 and $CaCO_3$ 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.

$CO_{2(g)} \rightleftharpoons CO_{2(aq)}$	$K_0 = \frac{[CO_{2(aq)}]}{pCO_2}$
$CO_{2(aq)} + H_2O \rightleftharpoons H^+ + HCO_3^-$	$K_1 = \frac{[H^+][HCO_3^-]}{[CO_{2(aq)}]}$
$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$
$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$	$K_{sp} = [Ca^{2+}][CO_3^{2-}]$

It is also useful to introduce $\sum CO_2$, the total amount of dissolved inorganic carbon in the system, and Alkalinity, the amount of H^+ required to titrate DIC to neutrality:

$$\sum CO_2 = [CO_{2(aq)}] + [HCO_3^-] + [CO_3^{2-}]$$
$$\text{Alkalinity} = [HCO_3^-] + 2 \times [CO_3^{2-}]$$

These expressions do not depend directly on pH. Note that carbonate precipitation decreases $\sum CO_2$ by removing CO_3^{2-} from the system, whereas respiration of organic matter increases $\sum CO_2$ by adding $CO_{2(aq)}$ to the system. Precipitation also decreases Alkalinity by 2 units for each unit of CO_3^{2-} removed from the system.

Respiration of organic matter increases $[CO_{2(aq)}]$ and $\sum CO_2$. It will acidify the water, mainly through the equilibrium K_1 (Le Châtlier's principle says the reaction goes to the right), but also somewhat through K_2 as $[HCO_3^-]$ increases. Every unit increase in $[CO_3^{2-}]$ 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. CO_3^{2-} cannot be sourced from DIC without also adding $[H^+]$. Something else has to donate CO_3^{2-} in order to maintain equilibrium for K_2. That something is $CaCO_3$, which dissolves to meet the "demand" for CO_3^{2-}. We then arrive at a familiar idea, that the addition of $CO_{2(aq)}$ results in $CaCO_3$ dissolution.

Consider, then, what happens when $CaCO_3$ precipitates. $\sum CO_2$ decreases when CO_3^{2-} is removed as $CaCO_3$, 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 Châtlier's principle could push K_2 to the right (there is not enough CO_3^{2-}), but that would exacerbate the $[H^+]$ problem. The only way to rebalance the DIC pool is to react H^+ with HCO_3^-. There is thus a further drop in $\sum CO_2$ through CO_2 release. Henry's law still applies, so the increase in $[CO_{2(aq)}]$ from $CaCO_3$ precipitation also ends up increasing pCO_2.

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