Carbonate equilibria in solutions exposed to the atmosphere I

Reactions in carbonate equilibria in a dilute solution:

\[ \text{CO}_2(g) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3^* \quad \text{pK} = 1.5 \]
\[ \text{H}_2\text{CO}_3^* \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \quad \text{pK} = 6.3 \]
\[ \text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+ \quad \text{pK} = 10.3 \]

This diagram is an elaboration of Figure 4.3 of Stumm and Morgan's (1996) *Aquatic Chemistry* (3rd edn). Note that the diagram's colored lines are drawn to show concentrations in a dilute solution. Part II of this series will show a corresponding diagram drawn with pK values appropriate for seawater.
Reactions in carbonate equilibria in seawater:

\[
\begin{align*}
\text{CO}_2(\text{g}) + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{CO}_3^* \quad pK = 1.5 \\
\text{H}_2\text{CO}_3^* & \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \quad pK = 5.97 \\
\text{HCO}_3^- & \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+ \quad pK = 9.68
\end{align*}
\]

A silicate weathering reaction:

\[
4\text{H}_2\text{CO}_3 + \text{Mg}_2\text{SiO}_4 \rightleftharpoons 2\text{Mg}^{2+} + 4\text{HCO}_3^- + \text{Si(OH)}_4^0
\]

Precipitation of CaCO₃ provides a sink for DIC and thus limits increase in [CO₃²⁻] and pH in seawater and most lakes, except in lakes that have proportionately little Ca²⁺. Seawater: pH = 8.2; [CO₃²⁻] = 12 ppm; [Ca²⁺] = 411 ppm Alkali Valley: pH = 10.1; [CO₃²⁻] = 91,400 ppm; [Ca²⁺] = ~0 Honey Lake: pH = 9.7; [CO₃²⁻] = 8,020 ppm; [Ca²⁺] = ~0

Lake data are from Drever (1988) Table 11-1.

This diagram is an analog of Figure 4.3 of Stumm and Morgan's (1996) Aquatic Chemistry (3rd edn). However, note that the diagram's colored lines are drawn to show concentrations in seawater and were drawn using pK values appropriate to seawater, as taken from Table 5.12 of Millero (2001).