

Mineral Stability

a)

Albite to Kaolinite

$$\begin{aligned}\Delta_r G^\circ &= \sum \Delta_f G^\circ_{products} - \sum \Delta_f G^\circ_{reactants} \\ &= (\Delta_f G^\circ 2Na^+ + \Delta_f G^\circ Al_2Si_2O_5(OH)_{4(s)} + \Delta_f G^\circ 4H_4SiO_4(aq)) \\ &\quad - (\Delta_f G^\circ 2NaAlSi_3O_8(s) + \Delta_f G^\circ 2H^+ + \Delta_f G^\circ 9H_2O) \\ &= [-(2)261.5 - (1)3797.5 - (4)1307.8] - [-(2)3711.7 + (2)0 - (9)237.1] \\ &= 5.6\end{aligned}$$

Kaolinite to Gibbsite

$$\begin{aligned}\Delta_r G^\circ &= \sum \Delta_f G^\circ_{products} - \sum \Delta_f G^\circ_{reactants} \\ &= (\Delta_f G^\circ 2Al(OH)_{3(s)} + \Delta_f G^\circ 2H_4SiO_4(aq)) \\ &\quad - (\Delta_f G^\circ Al_2Si_2O_5(OH)_{4(s)} + \Delta_f G^\circ 5H_2O) \\ &= [-(2)1154.9 - (2)1307.8] - [-3797.5 - (5)237.1] \\ &= 57.6\end{aligned}$$

b)

Albite to Kaolinite

$$\begin{aligned}\log_{10} k &= \frac{-\Delta_r G^\circ}{2.303RT} \\ -\Delta_r G^\circ &= -5.6 \\ \log_{10} k &= -\frac{5.6}{5.708} \\ &= -0.981079 \\ k &= 10^{-0.9811}\end{aligned}$$

Kaolinite to Gibbsite

$$\begin{aligned}\log_{10} k &= \frac{-\Delta_r G^\circ}{2.303RT} \\ -\Delta_r G^\circ &= -57.6 \\ \log_{10} k &= -\frac{57.6}{5.708} \\ &= -10.0911 \\ k &= 10^{-10.0911}\end{aligned}$$

c)

$$\begin{aligned}k_{eq} &= \frac{[Na^+]^2[Al_2Si_2O_5(OH)_{4(s)}][H_4SiO_4]^4}{[NaAlSi_3O_8(s)]^2[H^+]^2[H_2O]^9} \\ &= \frac{\gamma_{Na^+}^2[Na^+]^2\gamma_{H_4SiO_4}^4[H_4SiO_4]^4}{\gamma_{H^+}^2[H^+]^2}\end{aligned}$$

$$\begin{aligned}k_{eq} &= \frac{[Al(OH)_{3(s)}]^2[2H_4SiO_4]^2}{[Al_2Si_2O_5(OH)_{4(s)}][H_2O]^5} \\ &= \gamma_{H_4SiO_4}^2[H_4SiO_4]^2\end{aligned}$$

d)

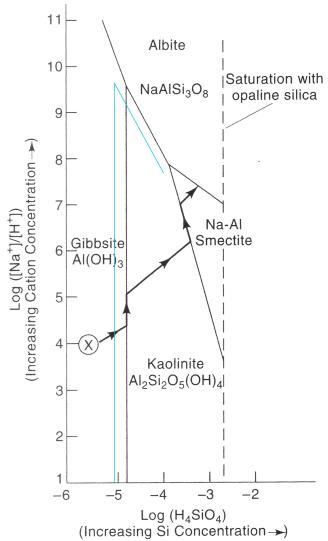
$$\begin{aligned}\log_{10} k_{eq} &= \log_{10} \left(\frac{\gamma_{Na^+}^2 [Na^+]^2 \gamma_{H_4SiO_4}^4 [H_4SiO_4]^4}{\gamma_{H^+}^2 [H^+]^2} \right) \\ &= \log_{10}(\gamma_{Na^+}^2 [Na^+]^2) + \log_{10}(\gamma_{H_4SiO_4}^4 [H_4SiO_4]^4) - \log_{10}(\gamma_{H^+}^2 [H^+]^2) \\ \log_{10} k_{eq} - \log_{10}(\gamma_{H_4SiO_4}^4 [H_4SiO_4]^4) &= \log_{10}(\gamma_{Na^+}^2 [Na^+]^2) - \log_{10}(\gamma_{H^+}^2 [H^+]^2) \\ \log_{10} \left(\frac{k_{eq}}{\gamma_{H_4SiO_4}^4 [H_4SiO_4]^4} \right) &= \log_{10} \left(\frac{\gamma_{Na^+}^2 [Na^+]^2}{\gamma_{H^+}^2 [H^+]^2} \right) \\ \log_{10} k_{eq} &= \log_{10}(\gamma_{H_4SiO_4}^2 [H_4SiO_4]^2)\end{aligned}$$

Assuming $\gamma = 1$,

$$\begin{aligned}\log_{10} \frac{[Na^+]}{[H^+]} &= -2 \log_{10}[H_4SiO_4] + 0.5 \log_{10} k_{eq} \\ &= -2 \log_{10}[H_4SiO_4] - 0.49\end{aligned}$$

$$\begin{aligned}2 \log_{10}[H_4SiO_4] &= \log_{10} k_{eq} \\ &= -10.1 \\ \log_{10}[H_4SiO_4] &= -5.05\end{aligned}$$

e)



The two lines intersect at (5.05, 9.61). The general shapes and trends of the lines agree, but the absolute offset is most likely due to differences in values used in the computation.

f)

Weathering albite into smectite would require an increase in proton concentration and a decrease in silicic acid concentration. Further weathering into kaolinite can be achieved by a combination of pH increase and decrease in silicic acid. Weathering of kaolinite to gibbsite is only dependent on a decrease in silicic acid.

g)

Though a process may be thermodynamically favorable and spontaneous, the process may be kinetically very slow. It would be very impractical to measure the concentrations of the different ions at many different points to experimentally build a stability diagram, especially if the system is kinetically slow and takes a long time to reach equilibrium. It may also be difficult to quantitatively measure the boundaries in a laboratory setting.

Carbonate System Bjerrum Plots

a)
Given

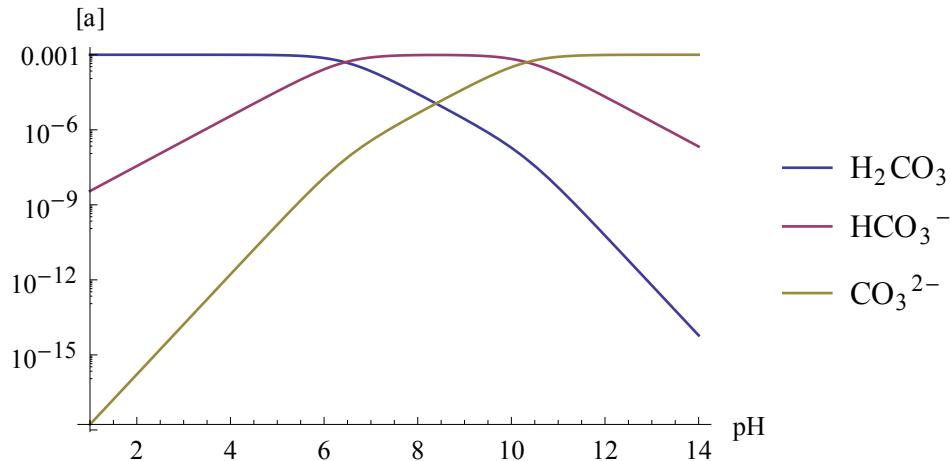
$$\begin{aligned}
 [CO_3^{2-}] &= \frac{C_T}{\alpha_H} \\
 [HCO_3^-] &= \frac{C_T[H^+]}{k_2\alpha_H} \\
 [H_2CO_3] &= \frac{C_T[H^+]^2}{k_1k_2\alpha_H} \\
 \alpha_H &= \frac{[H^+]^2}{k_1k_2} + \frac{[H^+]}{k_2} + 1 \\
 C_T &= [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \\
 k_1 &= \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \\
 k_2 &= \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}
 \end{aligned}$$

Substituting

$$\begin{aligned}
 [CO_3^{2-}] &= \frac{C_T}{\alpha_H} \\
 &= \frac{[H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]}{\frac{[H^+]^2}{k_1k_2} + \frac{[H^+]}{k_2} + 1} \\
 &= \frac{[H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]}{\frac{[H^+]^2}{[H^+][HCO_3^-]/[H_2CO_3]([H^+][CO_3^{2-}]/[HCO_3^-])} + \frac{[H^+]}{[H^+][CO_3^{2-}]/[HCO_3^-]} + 1} \\
 &= [CO_3^{2-}]
 \end{aligned}$$

b)

Carbonate Bjerrum Plot

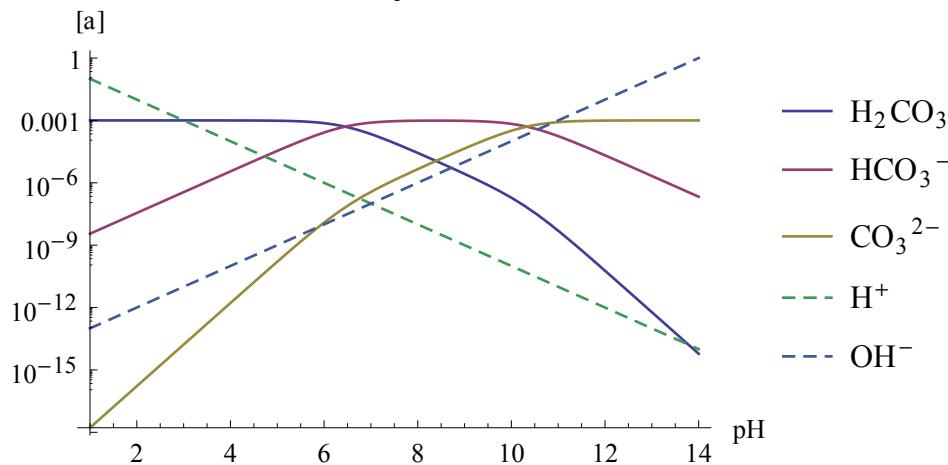


c)

$$\begin{aligned}[H^+][OH^-] &= 10^{-14} \\ [H^+] &= \frac{10^{-14}}{[OH^-]} \\ -pH &= -14 - \log_{10}[OH^-] \\ pH &= 14 + \log_{10}[OH^-]\end{aligned}$$

d)

Carbonate Bjerrum Plot

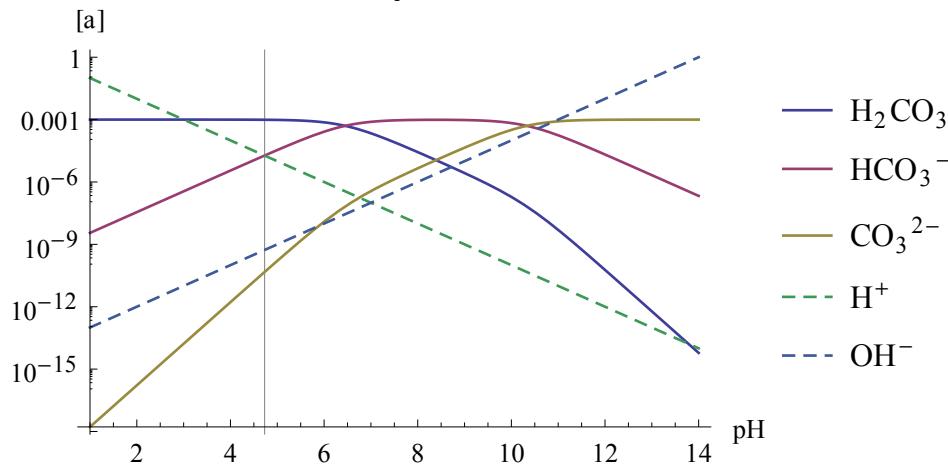


e)

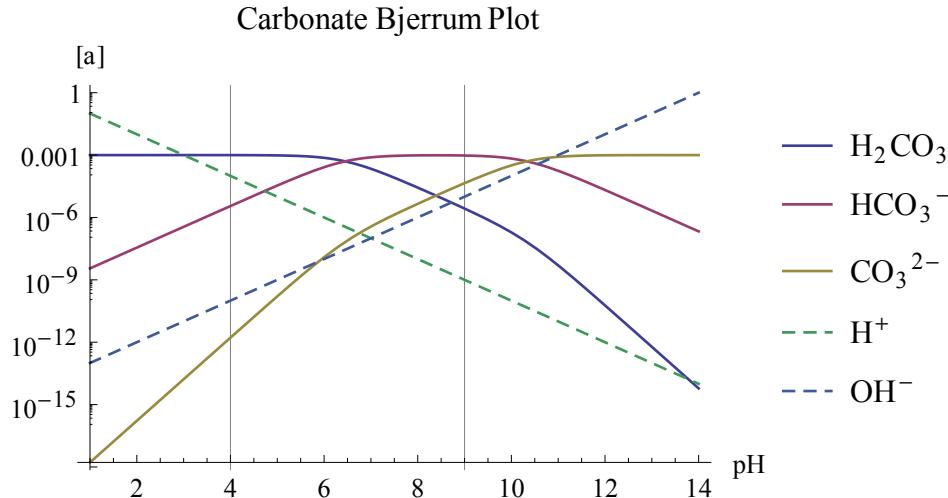
$$\text{Alkalinity} = [HCO_3^-] + 2[CO_3^{2-}]$$

The endpoint of carbonate alkalinity is pH 4.73 where bicarbonate concentration is equal to the proton concentration.

Carbonate Bjerrum Plot



f)



In water with a normal pH range, the major charged species of the carbonate system is the bicarbonate ion, and so it is by far the most dominant factor in determining alkalinity. This is no longer the case in very basic waters (above pH 10.33), where the carbonate ion concentration exceeds that of the bicarbonate.

g)

From class,

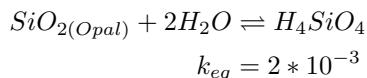
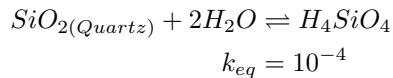
$$\begin{aligned}\log_{10} k_1 - \log_{10} a_{\text{H}^+} &= \log_{10} a_{\text{HCO}_3^-} - \log_{10} a_{\text{H}_2\text{CO}_3} \\ \log_{10} a_{\text{HCO}_3^-} &= -\log_{10} a_{\text{H}^+} - \log_{10} a_{\text{H}_2\text{CO}_3} - \log_{10} k_1 \\ y &= mx + b \\ m &= -1 \\ |m| &= 1\end{aligned}$$

By extension,

$$\begin{aligned}\log_{10} k_2 - \log_{10} a_{\text{H}^+} &= \log_{10} a_{\text{CO}_3^{2-}} - \log_{10} a_{\text{HCO}_3^-} \\ \log_{10} a_{\text{HCO}_3^-} &= \log_{10} a_{\text{CO}_3^{2-}} - \log_{10} k_2 + \log_{10} a_{\text{H}^+} \\ -\log_{10} a_{\text{H}^+} - \log_{10} a_{\text{H}_2\text{CO}_3} - \log_{10} k_1 &= \log_{10} a_{\text{CO}_3^{2-}} - \log_{10} k_2 + \log_{10} a_{\text{H}^+} \\ \log_{10} a_{\text{CO}_3^{2-}} &= -2 \log_{10} a_{\text{H}^+} + C \\ C &= -\log_{10} a_{\text{H}_2\text{CO}_3} - \log_{10} k_1 - \log_{10} a_{\text{CO}_3^{2-}} + \log_{10} k_2 \\ y &= mx + b \\ m &= -2 \\ |m| &= 2\end{aligned}$$

Silicic acid

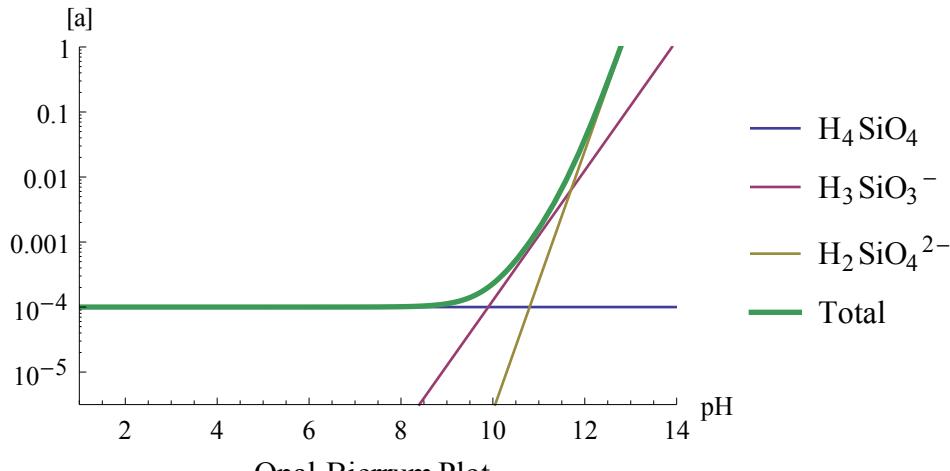
a)



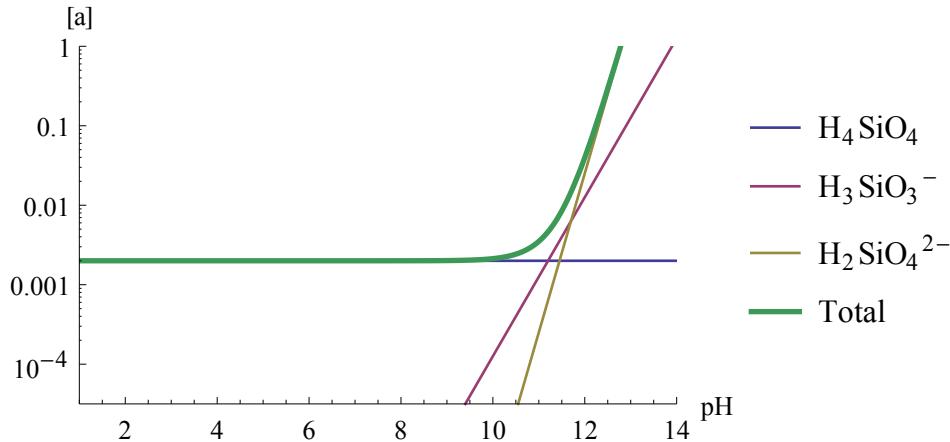
Analogous to the carbonate system,

$$\begin{aligned}
 Si_T &= [H_4SiO_4] + [H_3SiO_4^-] + [H_2SiO_4^{2-}] \\
 &= \alpha_H [H_4SiO_4] \\
 \alpha_H &= 1 + \frac{k_1}{[H^+]} + \frac{k_1 k_2}{[H^+]^2} \\
 k_1 &= 10^{-9.9} = \frac{[H^+][H_3SiO_4^-]}{[H_4SiO_4]} \\
 k_2 &= 10^{-11.7} = \frac{[H^+][H_2SiO_4^{2-}]}{[H_3SiO_4^-]} \\
 [H_4SiO_4] &= 10^{-4} | 2 * 10^{-3} = \frac{Si_T}{\alpha_H} \\
 [H_3SiO_4^-] &= \frac{k_1 Si_T}{\alpha_H [H^+]} \\
 [H_2SiO_4^{2-}] &= \frac{k_1 k_2 Si_T}{\alpha_H [H^+]^2}
 \end{aligned}$$

Quartz Bjerrum Plot



Opal Bjerrum Plot



pH calculation

From the text,

$$\begin{aligned} k_{sp(CaCO_3)} &= 10^{-8.3} \\ k_{1(H_2CO_3)} &= 10^{-6.4} \\ k_{2(HCO_3^-)} &= 10^{-10.3} \\ k_H &= 10^{-1.5} \\ pCO_2 &= 10^{-3.5} \text{ atm} \end{aligned}$$

Equilibrium constants,

$$\begin{aligned} k_1 &= \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \\ k_2 &= \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \\ k_{sp} &= [Ca^{2+}][CO_3^{2-}] \end{aligned}$$

Henry's Law,

$$[H_2CO_3] = k_H pCO_2$$

Substituting,

$$\begin{aligned} [CO_3^{2-}] &= \frac{k_2[HCO_3^-]}{[H^+]} \\ k_{sp} &= \frac{k_2[HCO_3^-][Ca^{2+}]}{[H^+]} \end{aligned}$$

Assuming pH will be near neutral, allowing us to cancel some terms,

$$\begin{aligned} mH^+ + 2mCa^{2+} &= mHCO_3^- + mOH^- \\ 2mCa^{2+} &= mHCO_3^- \\ mCa^{2+} &= \frac{1}{2}mHCO_3^- \end{aligned}$$

Substituting,

$$\begin{aligned} k_{sp} &= \frac{k_2[HCO_3^-]^2}{2[H^+]} \\ k_1 &= \frac{[H^+][HCO_3^-]}{k_H pCO_2} \\ [HCO_3^-] &= \frac{k_1 k_H pCO_2}{[H^+]} \end{aligned}$$

Further,

$$\begin{aligned} k_{sp} &= \frac{k_2 \left(\frac{k_1 k_H pCO_2}{[H^+]} \right)^2}{2[H^+]} \\ &= k_2 \frac{(k_1 k_H pCO_2)^2}{[H^+]^3} \\ [H^+]^3 &= k_2 \frac{(k_1 k_H pCO_2)^2}{k_{sp}} \\ [H^+] &= 10^{-8.36701} \\ pH &= 8.36 \end{aligned}$$