1. Carbonate Minerals

There are two main minerals that have the same chemical formula CaCO$_3$(s), calcite and aragonite.

The solubility reactions for each are written as (with equilibrium solubility constants $K_{so}$ at 25°C and 1 atm):

- CaCO$_3$(s) (calcite) = Ca$_2^+$ + CO$_3^{2-}$ \hspace{1cm} K'$_{so}$ = 10$^{-6.37}$
- CaCO$_3$(s) (aragonite) = Ca$_2^+$ + CO$_3^{2-}$ \hspace{1cm} K'$_{so}$ = 10$^{-6.19}$

a). Which is more soluble? (2)

Aragonite is more soluble because its solubility product constant ($K'$) is larger than the solubility product constant of calcite which means that at equilibrium more of the aragonite solid phase is dissolved than the calcite solid phase would be.

b). Write a reaction of CaCO$_3$(s) (calcite) going to CaCO$_3$(s) (aragonite) and find the equilibrium constant for this reaction. (5)

\[
\begin{align*}
CaCO_3(s) \text{ (calcite)} & \rightleftharpoons Ca^{2+} + CO_3^{2-} & K'_{so} = 10^{-6.37} \\
Ca^{2+} + CO_3^{2-} & \rightleftharpoons CaCO_3(s) \text{ (aragonite)} & K' = \frac{1}{K'_{so}} = 10^{-6.19} \\
CaCO_3(s) \text{ (calcite)} & \rightleftharpoons CaCO_3(s) \text{ (aragonite)} & K' = 10^{-6.37} \times 10^{-6.19} = 10^{-12.56}
\end{align*}
\]

c) If surface seawater has a pH = 8.0 and total CO$_2$ = 2.000 x 10$^{-3}$ mol kg$^{-1}$, what is the equilibrium concentration of dissolved CO$_3^{2-}$ ? Use pK$_1'$ = 6.0 and pK$_2'$ = 9.0. (10)

\[
\begin{align*}
H_2CO_3 & \rightleftharpoons H^+ + HCO_3^- \hspace{1cm} pK_1' = 6.0 \\
HCO_3^- & \rightleftharpoons H^+ + CO_3^{2-} \hspace{1cm} pK_2' = 9.0 \\
[H^+][HCO_3^-] & = K_1' \\
[H^+][CO_3^{2-}] & = K_2' \\
[H_2CO_3] & = K_1'[HCO_3^-] \\
\text{DIC} & = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3]
\end{align*}
\]

Rearrange the K equations to get [CO$_3^{2-}$] and [H$_2$CO$_3$] in terms of [HCO$_3^{-}$].

\[
\begin{align*}
[H_2CO_3] & = [H^+][HCO_3^-] / K_1' \hspace{1cm} \text{equation A} \\
[CO_3^{2-}] & = [HCO_3^-] * K_2' / [H^+] \hspace{1cm} \text{equation B} \\
\text{DIC} & = [[HCO_3^-] * K_2' / [H^+]] + [HCO_3^-] + [[H^+][HCO_3^-] / K_1'] \\
\text{DIC} & = [[HCO_3^-] * (10^{-9}) / (10^{-8})] + [HCO_3^-] + ([10^{-9}] * [HCO_3^-] / (10^{-6})} \\
\text{DIC} & = 0.11 * [HCO_3^-] + [HCO_3^-] + 0.01 * [HCO_3^-] = 1.11 * [HCO_3^-] \\
[HCO_3^-] & = \text{DIC} / 1.11 = (2.000 \times 10^{-3} \text{ mol l}^{-1}) / 1.11 = 1.80 \text{ mmol l}^{-1}
\end{align*}
\]

Now we know the concentration of [HCO$_3^{-}$] and we can use equation B to get [CO$_3^{2-}$].

\[
[CO_3^{2-}] = (1.80 \times 10^{-3} \text{ mol HCO}_3^- \text{ l}^{-1}) \times (10^{-9}) / (10^{-8}) = 1.80 \times 10^{-4} \text{ mol CO}_3^{2-} \text{ l}^{-1} = 180 \mu\text{mol CO}_3^{2-} \text{ l}^{-1}
\]
d) Using the equilibrium constants given above, if this surface seawater (with Ca$^{2+} = 10 \times 10^{-3}$ M) was in equilibrium with calcite, what would be the total concentration of CO$_3^{2-}$? (5)

\[
\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-} \quad \quad \quad K_{so} = 10^{-6.37}
\]

\[
K_{so} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]
\]

\[
[\text{CO}_3^{2-}] = \frac{K_{so}}{[\text{Ca}^{2+}]} = \frac{(10^{-6.37})}{(10 \times 10^{-3} \text{ mol l}^{-1})} = 10^{-4.37} = 4.26 \times 10^{-5} \text{ mol CO}_3^{2-} \text{ l}^{-1}
\]

\[
= 42.6 \mu \text{mol CO}_3^{2-} \text{ l}^{-1}
\]
2. Silicate reactions – Reverse Weathering

A proponent of "reverse weathering" has proposed that the minerals gibbsite, kaolinite and quartz exist together in equilibrium in the ocean according to the following reaction.

\[
\text{kaolinite} \quad \text{water} \quad \text{gibbsite} \quad \text{quartz} \\
H_4\text{Al}_2\text{Si}_2\text{O}_9 + H_2\text{O} = \text{Al}_2\text{O}_3\cdot3\text{H}_2\text{O} + 2 \text{SiO}_2
\]

The activity of water is defined in such a way that pure water has an activity of 1.0. If water has an activity of 0.90 that means that there is 90% water and 10% salt.

a) Calculate what the activity of water would be if these three solid phases were in equilibrium as described by this reaction. Below are the standard Gibbs Free Energies of formation for these phases. Remember that \(\Delta G_r^\circ = -2.3 \times RT \log K = -5.708 \log K\) (for \(G\) in kJ)

<table>
<thead>
<tr>
<th>Phase</th>
<th>(\Delta G_f^\circ) (kJ (\text{mol}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gibbsite</td>
<td>-1,155.0</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>-3,799.0</td>
</tr>
<tr>
<td>Quartz</td>
<td>-856.7</td>
</tr>
<tr>
<td>Water</td>
<td>-237.2</td>
</tr>
</tbody>
</table>

\[\Delta G_r^\circ = -1155 + 2(-856.7) - (-237.2) - (-3799) = +1167.8 \text{kJ mol}^{-1}\]

\[\log K = 1167.8 / -5.708 = -204.6\]

Thus \(K = 10^{-204.6}\)

b) Could this reaction be in equilibrium in seawater? Explain your answer.

If SW is 2.5% salt the activity of water in SW = 0.975
If we assume that the activity of the solids and only the activity of water can vary then:
\(Q = 1/0.975 = 1.025\)

As \(Q \neq K\) this reaction is not at equilibrium in SW.

So \(Q >> K\) and the reaction should go strongly to the left.
Kaolinite should form from gibbsite plus quartz
3. Carbonate System Calculations
Assume surface seawater has an alkalinity of 2.0 \times 10^{-3} and a total CO₂ of 2.0 \times 10^{-3}. Assume there is no borate contribution to the alkalinity. Assume K₁' = 10^{-6.0} and K₂' = 10^{-9.1}

a) What is the pH?

\[ \text{Alk} = \text{HCO}_3^- + 2 \text{ CO}_3^- \]
\[ \text{Alk} = C_T \alpha_1 + 2 C_T \alpha_2 \]
\[ \text{Alk} = C_T (\alpha_1 + 2 \alpha_2) \]

As Alk = C_T we have

\[ 1 = \alpha_1 + 2 \alpha_2 \]
\[ 1 = (H K_1 + 2 K_1 K_2) / (H^2 + H K_1 + K_1 K_2) \]
\[ H^2 + H K_1 + K_1 K_2 = H K_1 + 2 K_1 K_2 \]
Simplifies to:
\[ H^2 = K_1 K_2 = 10^{-6.0} \times 10^{-9.1} = 10^{-15.1} \]
\[ H^+ = 10^{-7.55} \]
\[ \text{pH} = 7.55 \]

b) What is the P_CO₂?

\[ \text{H}_2\text{CO}_3 = K_H \text{P}_{\text{CO}_2} \]
\[ C_T \alpha_1 = K_H \text{P}_{\text{CO}_2} \]
\[ \text{P}_{\text{CO}_2} = C_T \alpha_1 / K_H \]
\[ = \left(10^{2.7} / 10^{1.5}\right) \alpha_1 \]
\[ \alpha_1 \text{ at this pH simplifies to } H^2 / K_1 H \]
\[ = 10^{1.2} H/K_1 \]
\[ = 10^{1.2} \times 10^{-1.55} \]
\[ = 10^{2.75} = 1.78 \times 10^{-3} = 1780 \text{ ppm} \]

c) Is the P_CO₂ in this water in equilibrium with the atmosphere?

(P_CO₂ = 380 ppm = 10^{-3.420})

No - The surface seawater is supersaturated by \(10^{-2.75} / 10^{-3.42} = 10^{-0.67} = 4.7\text{x}\)
4) Thermodynamic versus Apparent Equilibrium Constants

Calcite (CaCO₃) is made into the shells of marine organisms in the surface ocean. The distribution of this material in marine sediments is correlated with depth. Deep-sea sediments, below a critical depth have no CaCO₃ while shallow sediments have close to 100% CaCO₃. For this problem I want you to calculate the degree of saturation (Ω) of CaCO₃ in surface seawater water using two different approaches. The information you need is given below. Please refer to Emerson and Hedges and my notes for all other values for parameters used in this calculation.

Calculate the degree of saturation (Ω) of calcite in surface seawater by two approaches. Assume that the concentration of total Ca is 1.04 x 10⁻² M and total CO₃²⁻ is 3.50 x 10⁻⁴ M

a) Use the thermodynamic equilibrium approach with the following values of ∆G°f. (10)

<table>
<thead>
<tr>
<th>species</th>
<th>∆G°f (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca²⁺</td>
<td>-553.54</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>-527.9</td>
</tr>
<tr>
<td>Calcite</td>
<td>-1128.8</td>
</tr>
</tbody>
</table>

b) Use the apparent equilibrium approach. Calculate the value of K' from equations 78 (calcite) in the paper by Millero (1995, Geochimica et Cosmochimica Acta 59, 661-677).(10)
In both cases surface seawater is supersaturated. But, the results differ by about a factor of two. The approach using the apparent equilibrium constants is better as those constants have been determined experimentally very precisely.