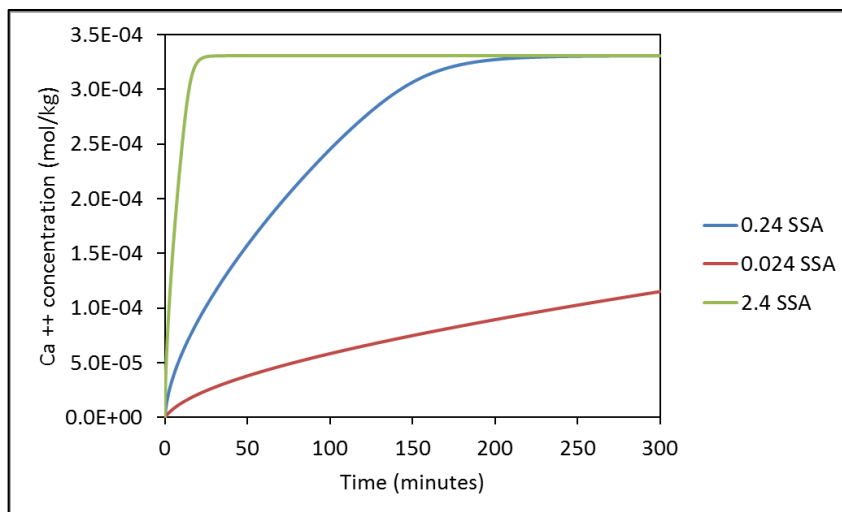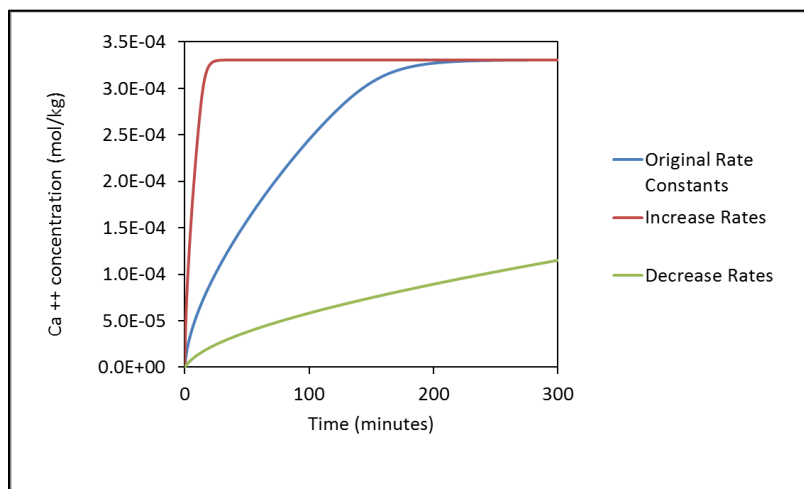PNG 550 hw#2

**Question 1. Carbonate Dissolution.**

1.  *Calcite specific surface area (SSA).* **In three different simulations, run the code using SSA being 0.024, 0.24, and 2.4 m$^2$/g. Plot the total Ca(II) as a function of time under these surface area values in one figure. Discuss how SSA affects calcite dissolution kinetics.**



The higher the specific surface area of the calcite, the faster the Ca(II) concentration increased or calcite dissolved. The 0.024 m^2/g specific surface area parameter was much slower in terms of reaching higher Ca(II) concentrations.
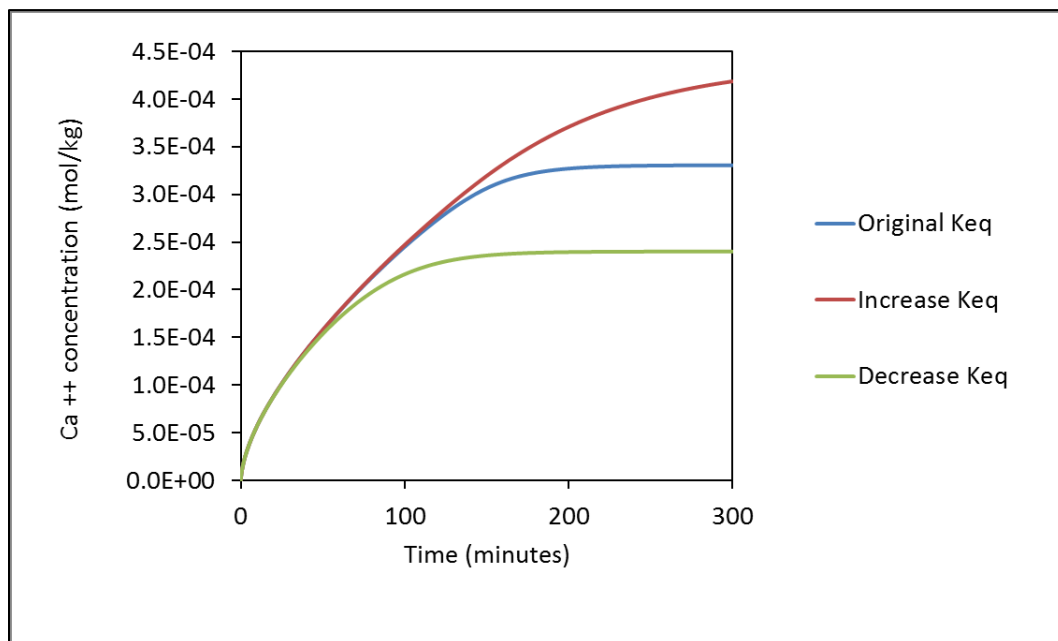
*2. Kinetic rate constant:* **increase and decrease the original three rate constant values in Example 1 by an order of magnitude. Compare the Ca(II) concentration evolution under the three k values in one figure. Also compare this figure here with the figure in 1) with the SSA of 0.24 m$^2$/g. Do changing k and A have the same impact on dissolution rates?**

In this case, the specific surface area was kept constant at the original 0.24 m^2/g and the rate constants were increased and decreased by an order of magnitude. The increased rate constants reached higher Ca(II) concentrations much more rapidly than did the situation where the rate constants were decreased. Changing the rate constants had the same impact on dissolution rates as did changing the SSA values.
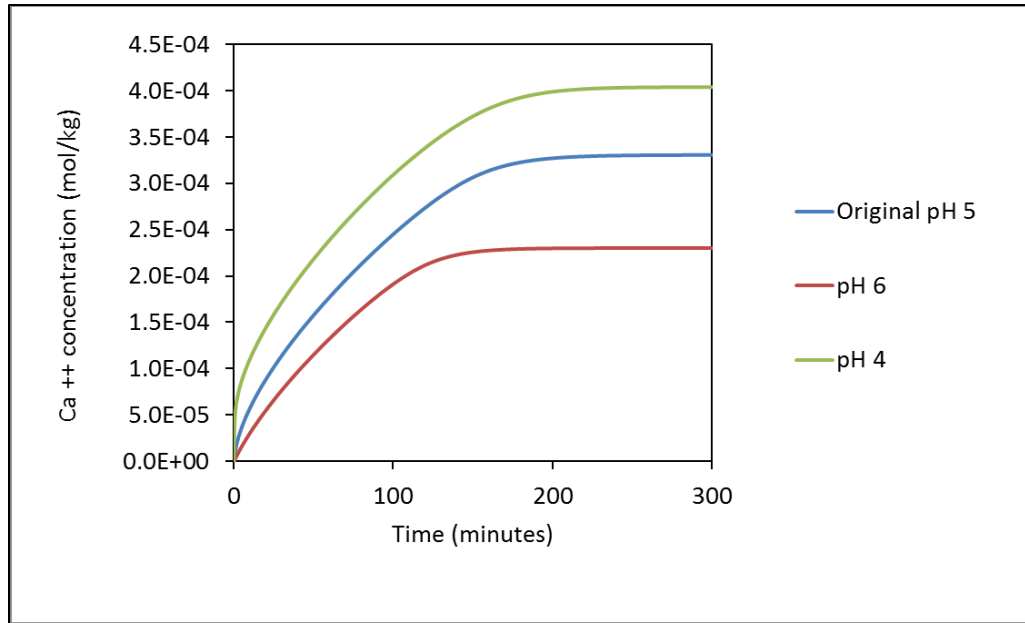
**3. Equilibrium constant $K_{eq}$ quantifies how much a mineral can dissolve in aqueous phase. Increase and decrease the equilibrium constant by an order of magnitude. Please plot the three curves (total Ca(II) ~ t) with different $K_{eq}$ values in one figure. What do the rate kinetics change with the total Ca(II) evolution figure?**

In this situation the SSA is 0.24 m^2/g and the rate constants are at their original values. Interestingly, though logically, the plot lines all reach a final approached Ca(II) concentration about a factor away from each other. For example the total Ca(II) concentration at the end of the 300 minutes is 2 times higher in the increased Keq situation as compared with the decreased Keq situation, though the Keq values are 2 orders of magnitude different.
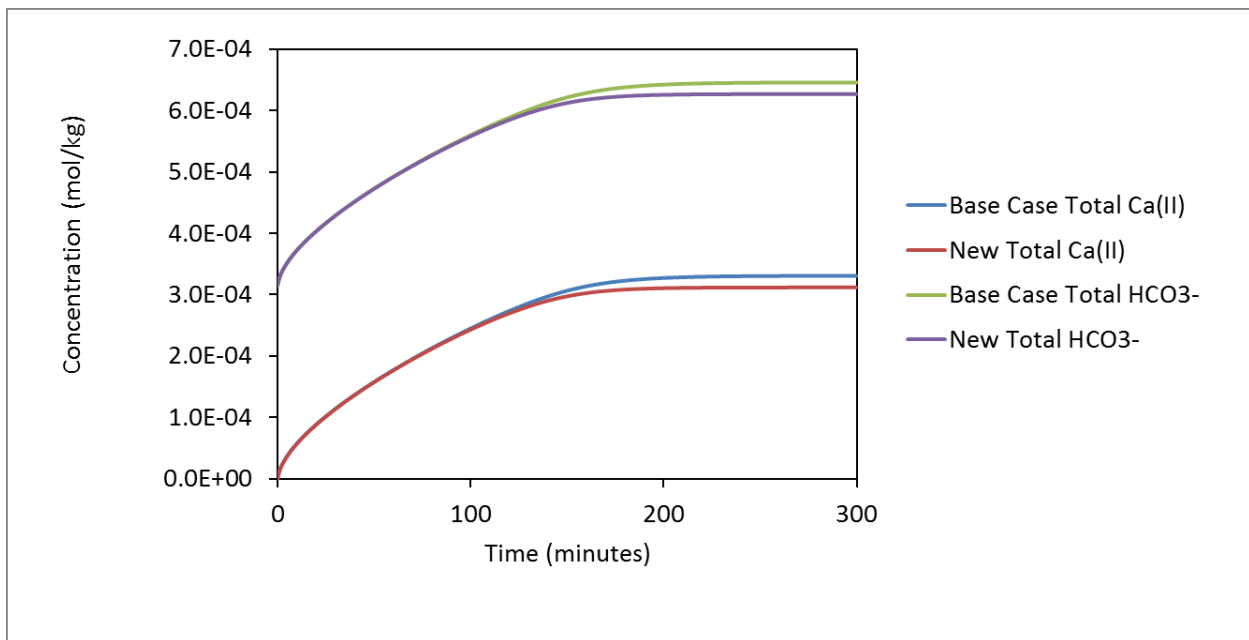


**4. Initial pH condition. Compare the base case with 2 more cases where you have the initial pH being 4.0 and 6.0.**

The higher the pH the slower the rate of calcite dissolution/decreased amount of total Ca(II) concentration. At a pH of 4 we can dissolve more calcite into solution than at a higher pH of 6.
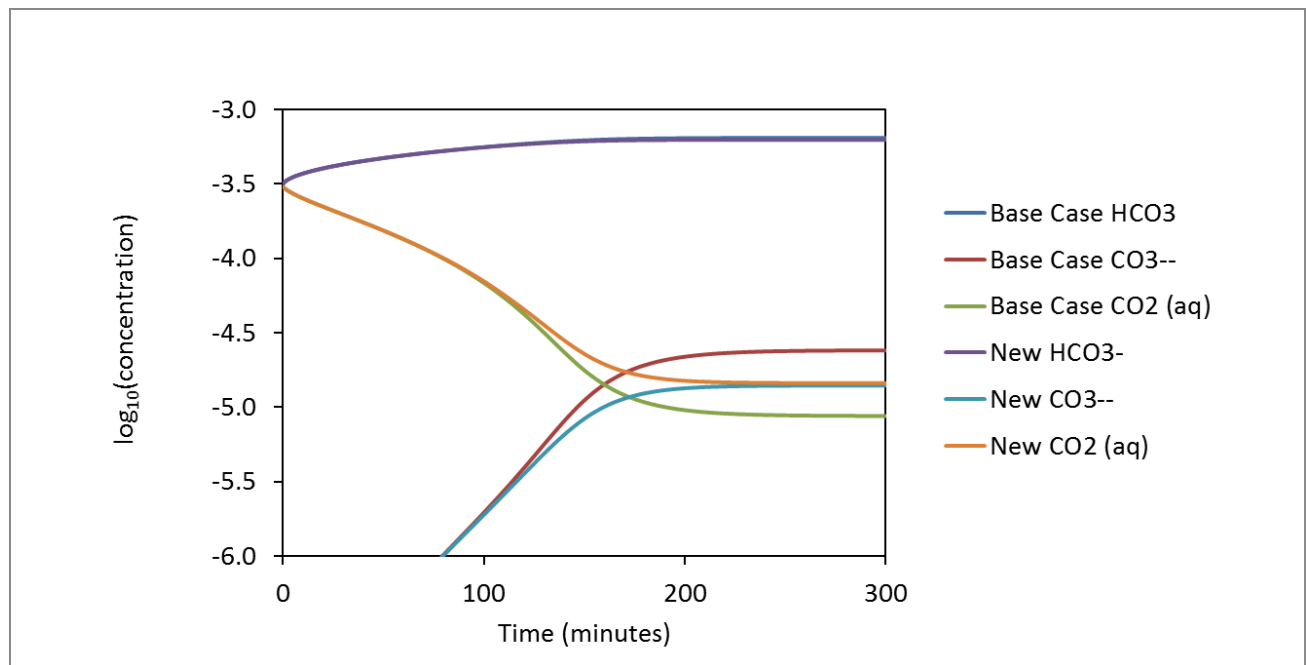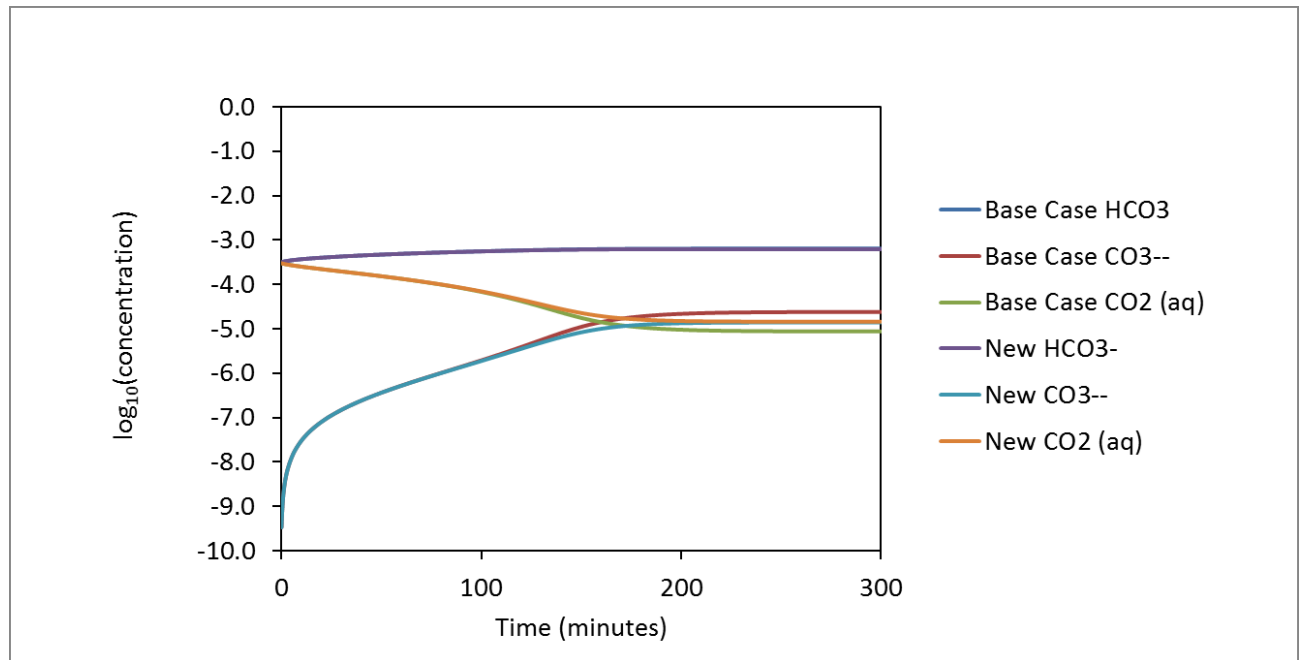
**5. The role of speciation. Remove all secondary calcium species and compare with base case scenario, Example 1 plots.**

1.  Total Ca(II) and total inorganic carbon;
2.  Individual Ca-containing species and carbonate species;
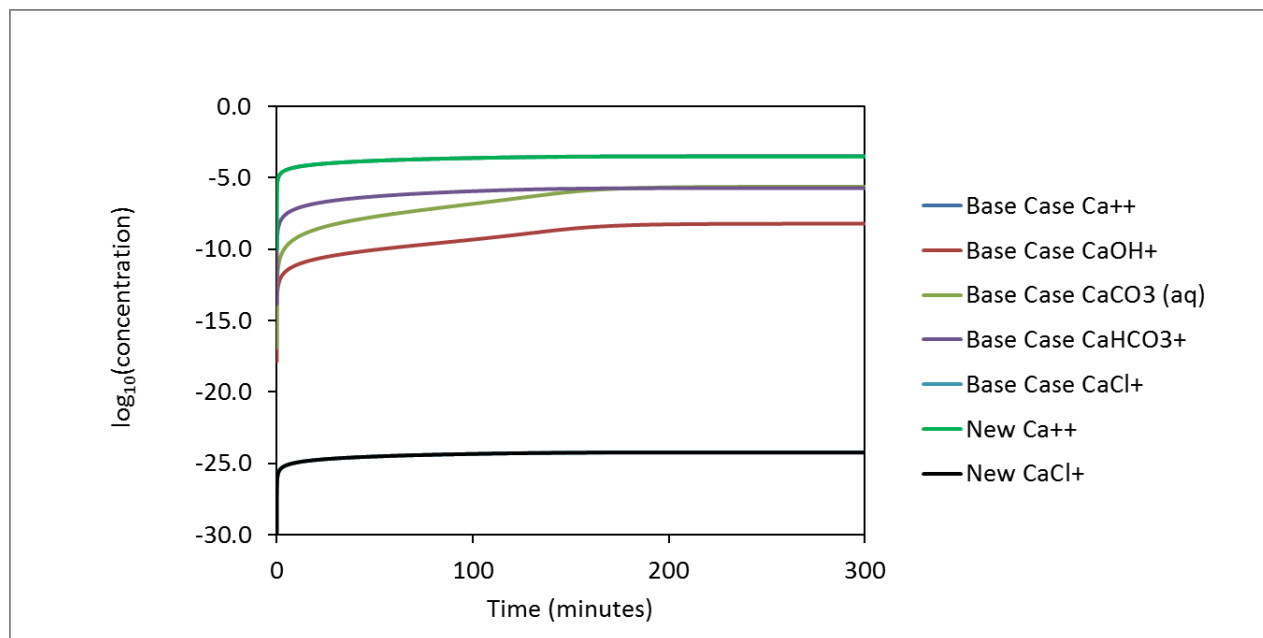3.  pH and the saturation index IAP/Keq



In this comparison of total Ca(II) and HCO3- (TIC), there is slightly higher concentrations of both Ca(II) and HCO3- in the original base case scenario when we allow the formation of additional calcium

speciation, which increases the dissolution of calcite since there are more avenues for it to "go" in solution.





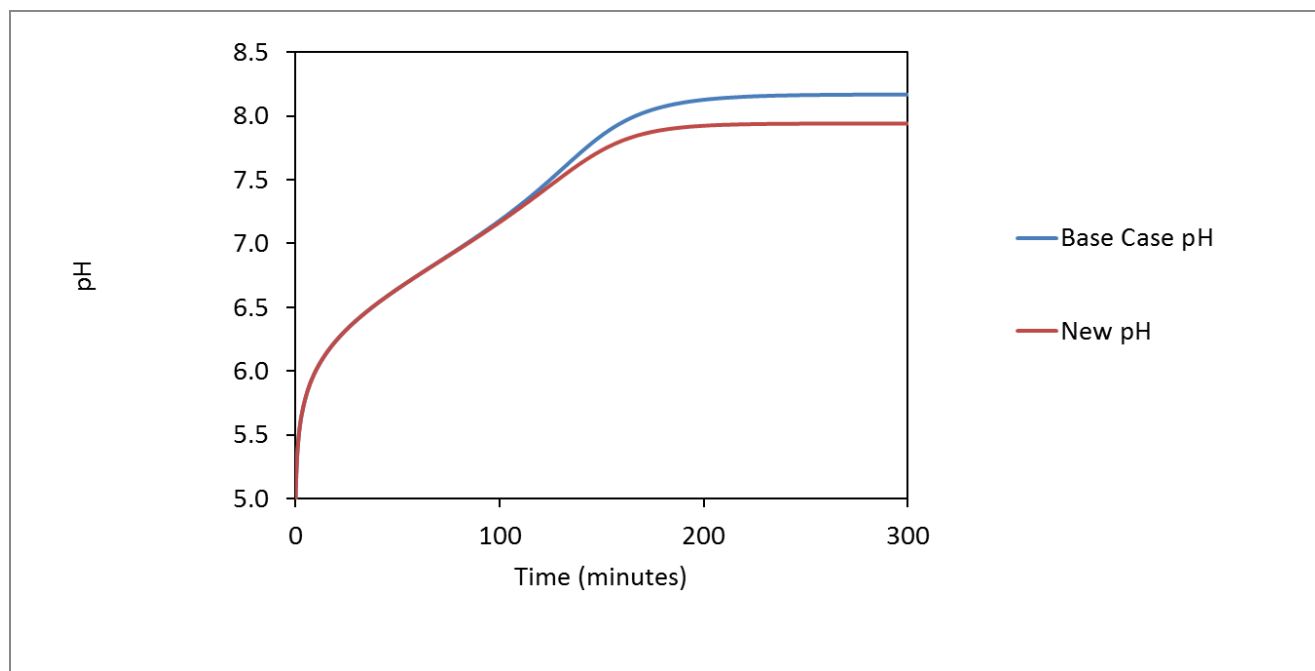Comparing the base case and new case with the removal of calcium speciation, we can see from these 2 plots with the second one zoomed in to see differences, that we have higher concentrations of CO2 (aq) in the new case, and lower concentrations of CO3--. This shows that the additional speciation will allow for better pH buffering of our system as the CO3—acts as a sink for protons and the CO2 (aq)
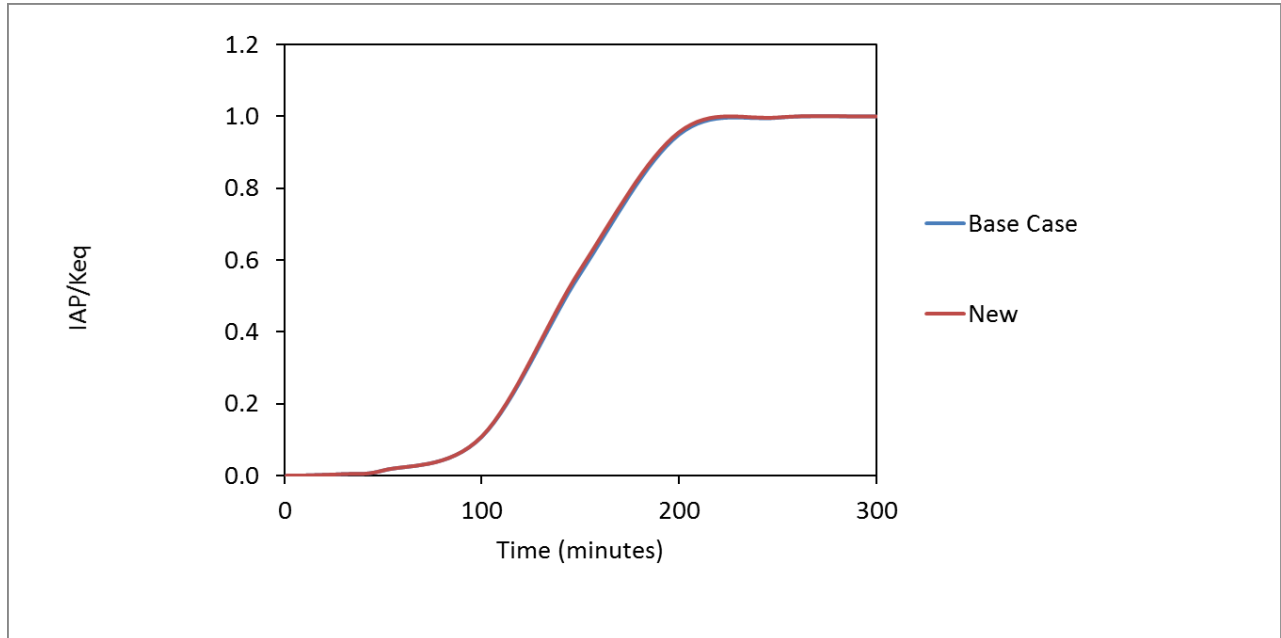
concentration indicates a lower pH. The concentration of HCO3- remains the same as the dissolution of the calcite is in a 1:1 stoichiometric ratio of Ca (II) and HCO3-.



The only difference between the base case and the new scenario without speciation is simply the existence of the additional species in the new case. The Ca++ and CaCl+ concentration profiles are exactly overlaid.
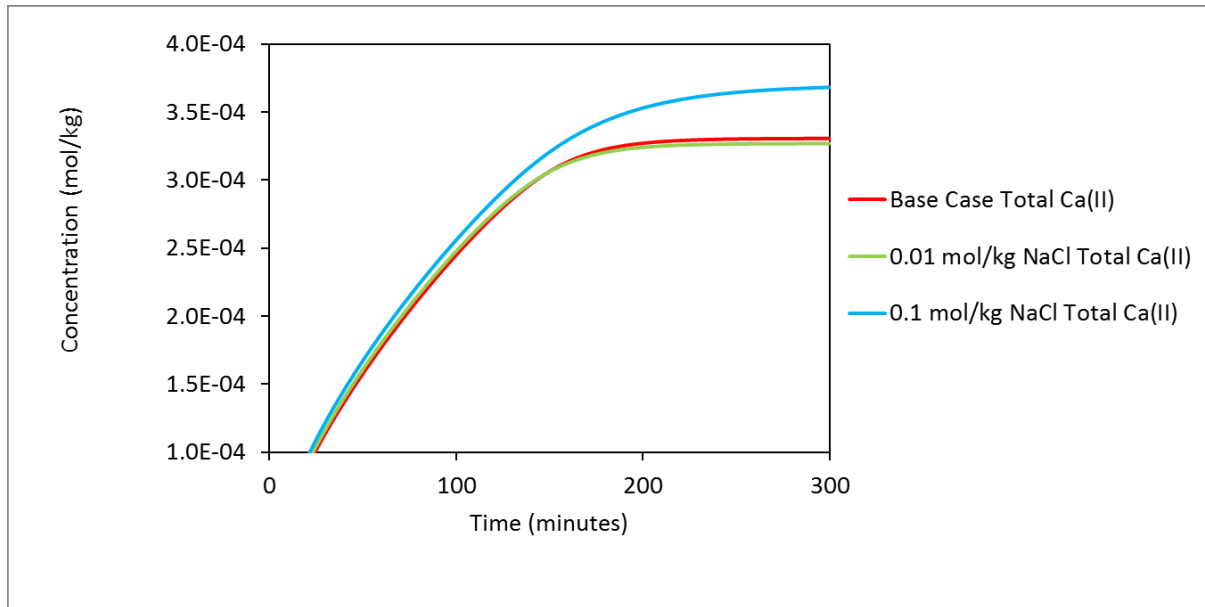
The pH, as expected, in the base case remains buffered slightly more than the new case without speciation. Tis is because the speciation allows for more and more dissolution of calcite into solution and the carbonate (CO3--) buffers pH by taking up protons in solution and increasing the pH. The new scenario has less buffering capacity due to the absence of more calcium species.



The IAP/Keq plot vs time for the base case and new scenario are exactly overlaid. And both reach a value of 1 at the end of the simulation, or equilibrium.

**6. Salinity. In the base case scenario there is no NaCl in solution. Simulate 2 more cases with NaCl at concentrations of 0.01 and 0.1 mol/kgw, respectively. Please compare total Ca(II) evolution under these 3 salinity conditions.**

In the following plot, comparing the 3 NaCl solutions for total Ca(II) in solution, at the initial time to around 150 minutes all 3 trendlines look about the same. However, after 150 minutes the 0.1 molg/kg NaCl solution has higher concentrations of total Ca(II) in solution, perhaps indicative of the ability for CaCl+ to form at this point.
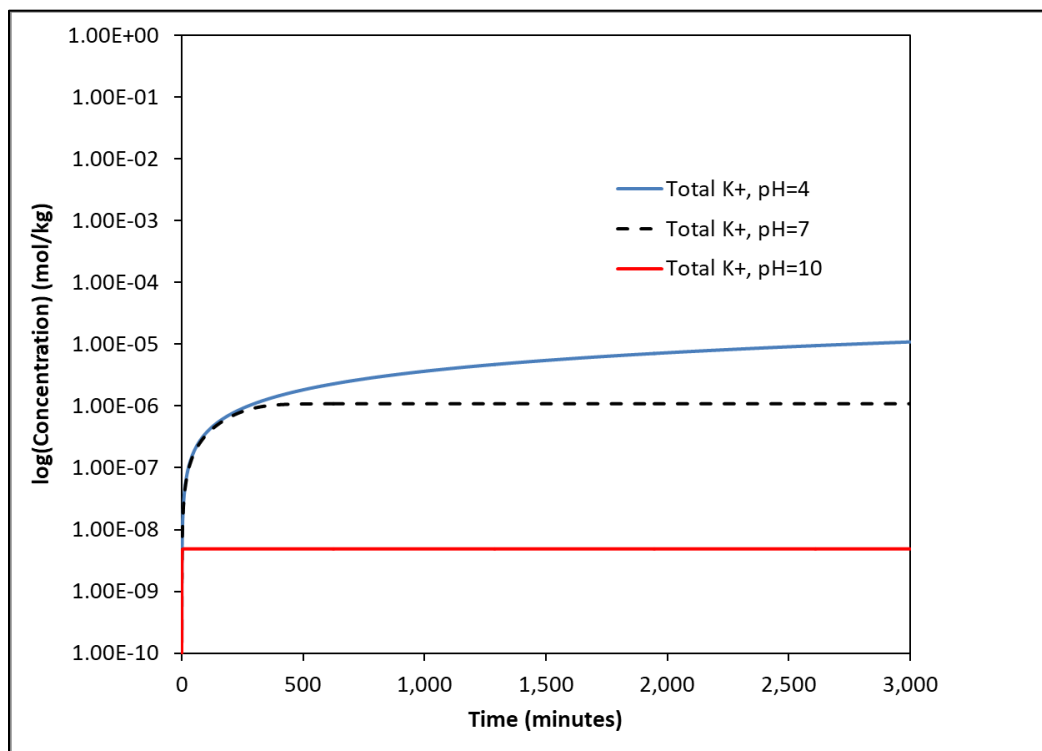
**7. Summarize observations from these questions. Which factors have the most significant control on calcite dissolution?**

Changing the specific surface area and kinetic rate constants had the largest effect on the visual trend vs time for Ca++ concentrations, however the Ca++ concentrations all eventually reached the same concentration in each scenario, it just took a longer period of time for the decreased rate and decreased surface area to reach the maximum concentration. In contrast, by altering pH and Keq the ultimate maximum Ca++ concentration possible was changed by 2 times between the lowest pH and highest pH condition and similarly for the shifted Keq. While the trends were essentially identical, the trends were shifted up and down from baseline. Speciation of calcium and lack thereof amounted to a near negligible difference between free calcium in solution in each case. The addition if increasing salinity may have had the smallest effect on Ca(II) concentrations in each respective solution. In terms of this 300 minute length of time, changing the specific surface area and kinetic rate constants affected the final concentrations in the lowest value plots for each parameter with a 3 times concentration difference between the low condition value and the high at the end of 300 minutes. However, on a larger scale, if time continued, the most significant effect on the amount of calcite that could be dissolved would be the altering of the Keq and pH which changed the total amount of Ca(II) that could potentially be dissolved into solution.

**Optional Question 2. Feldspar Dissolution.**

The feldspar mineral I chose was K-Feldspar as it already had the required mineral blocks created within the database. I could not access the given research article but instead found specific surface area data from Peckhaus et al 2016 of an estimated 2.64 m^2/g for an 80% K-Feldspar mineral measured. Bevan and Savage 1989 contained kinetic rate constants experimentally determined for K-Feldspar or orthoclase. At low pH of around 1 the rate constants at 25C was 1.4E-11 mol/(m^2-s), at a pH of 5 it was 1.67E-12, and for a pH of 9 there was no observed rate of increase in dissolution from the range of pH4-9. This observation was interesting because it went against other findings in literature that feldspar dissolution rates increase with increasing OH- concentrations at higher pH values. There were experimental limitations noted. So I used the same rate constant for alkaline conditions as the pH=5 for modeling convenience.

The following plot is the concentration of K+ ions vs time of up to 3000 minutes. Interestingly, according to the data, K-Feldspar dissolution decreases with increasing pH which is against what was noted in the literature. However, in the Bevan and Savage 1989 paper dissolution of K-Feldspar increased with the presence of oxalic acid so this could be correct based on those kinetic rate constants from that study.



SSA data: https://www.atmos-chem-phys.net/16/11477/2016/acp-16-11477-2016.pdf

Kinetic rate constants: http://www.minersoc.org/pages/Archive-MM/Volume_53/53-372-415.pdf