Dissolution Of Minerals in Water

To instructors

The purpose of this lab is to illustrate the nature of mineral dissolution in water. Many experiments have used buffered solutions, but for a number of reasons this exercise uses deionized water. The idea is that each student does a simple model chemical weathering system. There are four goals:

1. To characterize and balance the dissolution reaction.
2. To calculate (an imperfect) equilibrium constant for the reaction.
3. To fit a curve to the concentration of dissolved components with time.
4. To estimate the saturation concentration of the dissolved components.

The sample preparation and starting of this experiment takes about 1 three-hour lab period, including taking of the first sample after 1 hour.

The exercise handout

The fact that surface water starts out as very pure rain or snow, and ends up as salt-laden ground and surface water (typically 20 to 200 ppm total dissolved solids) demonstrates that minerals dissolve in water. It has also been shown that ancient ground water tends to have a higher dissolved solids content than young ground water, indicating that equilibrium is reached slowly. In this lab we will examine the dissolution of several different minerals in deionized water:

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Group</th>
<th>Basic formula</th>
<th>Approximate actual formula*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albite</td>
<td>Feldspar</td>
<td>NaAlSi$_3$O$_8$</td>
<td>(Na$<em>{0.90}$K$</em>{0.06}$Ca$<em>{0.04}$)Al$</em>{1.04}$Si$_{2.96}$O$_8$</td>
</tr>
<tr>
<td>Biotite</td>
<td>Sheet silicate</td>
<td>KMg$_3$Si$<em>3$AlO$</em>{10}$(OH)$_2$</td>
<td>(K$<em>{0.9}$Na$</em>{0.05}$)(Mg$<em>{1.5}$Fe$</em>{1.3}$Al$<em>{0.2}$)(Si$</em>{2.8}$Al$<em>{1.2}$)O$</em>{10}$(OH)$_2$</td>
</tr>
<tr>
<td>Calcite</td>
<td>Carbonate</td>
<td>CaCO$_3$</td>
<td>(Ca$<em>{0.99}$Mg$</em>{0.01}$)CO$_3$</td>
</tr>
<tr>
<td>Crysotile</td>
<td>Sheet silicate</td>
<td>Mg$_3$Si$_2$O$_5$(OH)$_4$</td>
<td>(Mg$<em>{2.7}$Fe$</em>{0.3}$)Si$_2$O$_5$(OH)$_4$</td>
</tr>
<tr>
<td>Dolomite</td>
<td>Carbonate</td>
<td>CaMg(CO$_3$)$_2$</td>
<td>Ca(Mg$<em>{0.98}$Fe$</em>{0.02}$)(CO$_3$)$_2$</td>
</tr>
<tr>
<td>Labradorite</td>
<td>Feldspar</td>
<td>(Ca,Na)(Al,Si)$_4$O$_8$</td>
<td>(Ca$<em>{0.5}$Na$</em>{0.5}$)(Al$<em>{1.5}$Si$</em>{2.5}$)O$_8$</td>
</tr>
<tr>
<td>Muscovite</td>
<td>Sheet silicate</td>
<td>KAl$_2$Si$<em>3$AlO$</em>{10}$(OH)$_2$</td>
<td>(□$<em>{0.1}$K$</em>{0.8}$Na$_{0.1}$)Al$_3$Si$<em>3$O$</em>{10}$(OH)$_2$</td>
</tr>
<tr>
<td>Olivine</td>
<td>Orthosilicate</td>
<td>Mg$_2$SiO$_4$</td>
<td>(Mg$<em>{1.8}$Fe$</em>{0.2}$)SiO$_4$</td>
</tr>
<tr>
<td>Orthoclase</td>
<td>Feldspar</td>
<td>KAlSi$_3$O$_8$</td>
<td>(K$<em>{0.9}$Na$</em>{0.1}$)AlSi$_3$O$_8$</td>
</tr>
<tr>
<td>Ankerite**</td>
<td>Carbonate</td>
<td>(Fe,Mg,Ca)CO$_3$</td>
<td>(Fe$<em>{0.5}$Mg$</em>{0.25}$Ca$_{0.25}$)CO$_3$</td>
</tr>
<tr>
<td>Talc</td>
<td>Sheet silicate</td>
<td>□Mg$_3$Si$<em>4$O$</em>{10}$(OH)$_2$</td>
<td>□(Mg$<em>{2.7}$Fe$</em>{0.3}$)Si$<em>4$O$</em>{10}$(OH)$_2$</td>
</tr>
<tr>
<td>Tremolite</td>
<td>Amphibole</td>
<td>□Ca$_2$Mg$_5$Si$<em>8$O$</em>{22}$(OH)$_2$</td>
<td>□Ca$<em>2$(Mg$</em>{4.8}$Fe$_{0.2}$)Si$<em>8$O$</em>{22}$(OH)$_2$</td>
</tr>
<tr>
<td>Wollastonite</td>
<td>Chain silicate</td>
<td>CaSiO$_3$</td>
<td>CaSiO$_3$</td>
</tr>
</tbody>
</table>

* For information purposes; do not use these in your calculations unless they are determined to be reasonable, or if you have no other chemical constraints.
Sample preparation

1. Crush the sample and sieve to capture 5 ±0.5 g of sample in the size range 0.25 to 1 mm. Collect only 2 ±0.2 g of the sheet silicates, with no sieving. Muscovite and biotite must be cut with scissors into 5 mm size pieces. Talc should be scraped off with a metal spatula or knife. Serpentine is best left in chunks. Don't fuzz it up.
2. Optional: Examine the sample under a stereo microscope and remove contaminants.
3. Put your sample into a 125 ml plastic bottle.
4. Add ~50 ml of 1% Citranox® detergent in deionized water and ultrasonically clean for 2 or 3 minutes. Decant the fines and rinse a couple of times.
5. Despite step 4, there still are small particles adhering to the mineral surfaces, and damaged regions on the crystals. These need to be removed or the dissolution rate and reaction may not be regular. Add the acid solution suitable for your sample, and rinse the outside of the bottle with DI water. Shake for 5 minutes, then decant the acid. Note warnings for HF.
6. Rinse the sample a minimum of ten times in deionized water after the second etch. Don't forget to rinse the outside of the bottle and bottle cap and threads. DON'T pour out your sample!
7. Add a final ~100 ml of deionized water (to mark). Cap the bottles and put them on their sides in a drying oven at 50ºC.

Running the experiment

1. Periodically gently shake the samples. Take one sample after 1 hour, I will take a sample tomorrow morning, and we will take additional samples during each of the next class meetings to the next lab. We will assume that the rate limiting dissolution step is surface reaction rather than diffusion or convection of dissolved components away from the water-mineral interface. In general this is a good assumption for our slow-to-dissolve minerals.
2. At several intervals (e.g., 1 day, 2 days, 4 days, 7 days), remove the samples from the drying oven and cool them to room temperature.
3. With a syringe take 6 ml of water from each sample and filter through a 0.2 mm filter; 2 ml into each of 2 ion chromatograph sample tubes, and 1 ml into an ICP-MS test tube. The 1 ml should be as accurate as you can get it using the syringe. Return the samples to the drying oven to continue reacting.

Analysis

1. Analyze the ion chromatograph autosampler tube samples for cations according to the ion chromatograph instructions.
2. Analyze the ICP-MS test tube samples for Al and Fe according to the ICP-MS water analysis instructions.

Data reduction

1. Calculate the detection limits and the usual statistics on the analyses, where data make that possible.
2. Subtract the blanks from the analyzed samples.
3. Determine the elements of interest in your sample (table above, but also consider other elements having concentrations above the detection limit). Ignore the other elements. Calculate the molar concentration of each element of interest in your solution. If possible, use the last day sample pH to determine if H⁺ or OH⁻ ions were produced during reaction.

Balanced dissolution reaction (use the last collected samples only)

1. Determine that the minerals are dissolving into solution. If so, are they undergoing congruent or incongruent dissolution? You may make the initial assumption that Na, Ca, Mg, and K go into solution without precipitating. This will have to be substantiated in some way eventually.
2. If your mineral allows it, check that the ratios of these elements in solution (molar units) are reasonable for your mineral, which will confirm that they are going into solution in reasonable proportions. Next, see if other elements (such as Si, Fe, and Al) are entering solutions in the same proportions as they would if the mineral were dissolving congruently. If these elements have low concentrations, that suggests that they are precipitating.
3. Calculate the dissolution reaction and balance it, including H₂O, H⁺, and OH⁻ as necessary. You may have to include some species that we did not analyze for, such as HCO₃⁻. For the balancing, you have two choices: using the Solver program in Excel, or by hand. By hand is not so hard as it may seem. An easy way to balance the reaction is to reduce the complex mineral to simple compounds, and write an appropriate dissolution reaction for each compound. Then add the simple reactions together. For example, sodium silicate can dissolve to unknown products: Na₂SiO₃ = ?. This compound, and parts of the dissolution reaction, can be broken down into the hypothetical one-metal components Na₂O and SiO₂. Each of these can dissolve in water, producing two partial hypothetical reactions, which are then added together:

   This partial reaction: \( \text{Na}_2\text{O} + \text{H}_2\text{O} = 2\text{Na}^+ + 2\text{OH}^- \)
   
   Plus this partial reaction: \( \text{SiO}_2 + 2\text{H}_2\text{O} = \text{H}_4\text{SiO}_4 \)

   Gives this whole reaction: \( \text{Na}_2\text{SiO}_3 + 3\text{H}_2\text{O} = 2\text{Na}^+ + \text{H}_4\text{SiO}_4 + 2\text{OH}^- \)
4. Calculate the solubility product constant of the reaction, assuming that the dissolution has attained equilibrium. Again, use the last set of samples collected to do this. Comment on the likelihood that dissolution equilibrium has been attained.

**Approach to equilibrium**

1. Make one graph showing the concentration in solution of the one chemical component analyzed that was the most concentrated. Do not include H⁺, OH⁻, and other species that were not analyzed. The Y axis should be molarity and the X axis should be time in hours. Assume zero concentration at time = 0 as one point on your graph. In general the graph will show concentration increasing with time at an ever decreasing rate, indicating gradual approach to equilibrium.

2. On the graph plot a best-fit curve to the data including the point at time = 0. Conceptually, this curve should pass through the origin, and become asymptotic to the saturation concentration of the plotted component. Unfortunately, typical spreadsheets have no curve options that fit these constraints. A hyperbolic curve of the following form will fit the data, however:

\[
Y = \alpha \left(1 - \frac{1}{\frac{X}{b} + 1}\right)
\]

In which Y is molar concentration of an element at time X, and a and b are constants. You can set this equation up and solve for constants a and b using the Solver function, by trying to set the sum of the squares of the residuals to zero. Here is an example of how to do this.

**What to turn in**
• A table showing the important parts of the analytical data and statistics.
• A brief commentary on analytical precision and detection limits for different elements.
• A balanced dissolution reaction, with a description of evidence supporting it.
• A solubility product constant for your mineral, with the constant expression shown.
• A graph showing how one chemical component concentration changes. Include some commentary on evidence that equilibrium was or was not approached.

Notes

Things needed for this lab

- It is very important that the minerals be quite pure, and in particular they should be free of phases that are more easily dissolved than the mineral of interest. Quartz in calcite, for example, is OK, but calcite in dolomite is not.
- One mineral sample for each student, ~12 g, crushed and sieved to 0.35-1 mm size before or during lab.
- One 125 ml plastic bottle for the dissolution experiments.
- Safety equipment (goggles, lab coats, aprons, rubber gloves).
- Plastic weighing boats.
- Autosampler test tubes (set for ion chromatograph, set for ICP-MS).
- Ultrasonic cleaners.
- 2 pint bottle of 2% acetic acid in a hood.
- 2 pint bottles of 5% HCl in a hood.
- 2 pint bottles of 5% HCl / 2% HF in a hood.
- Minimum of one liter bottle of deionized water per student for washing.
- Syringe filter apparatus, 0.2 mm pore size.

Maximum expected concentrations, ppm:

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>K</th>
<th>Ca</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1997</td>
<td>7</td>
<td>39</td>
<td>0.2</td>
<td>107</td>
<td>1.6</td>
<td>44</td>
<td>0.3</td>
</tr>
<tr>
<td>2001</td>
<td>2</td>
<td>14</td>
<td>0.1</td>
<td>22</td>
<td>0.3</td>
<td>18</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Ion chromatograph notes

An ion chromatograph is not essential for this lab. Na, Mg, K, and Ca concentrations, for some minerals, will approach routine (non-pre concentration) detection limits of 0.01-0.05 ppm. This is most notably the case for muscovite. If you have a suitably fancy ICP-MS instrument with analytical modes that decrease detection limits for K and Ca, then by all means use the ICP-MS for all elements of interest.

ICP-MS notes

Use no acid for the analyzed solutions, blanks, or standards! All solutions, including the between-sample rinse solution, should be DI water. Here are instructions for mixing the solutions:

<p>| Unknowns: | Unknowns test tubes originally have 1 ml of sample. Pipette out 0.5 ml, discard the rest, and put the 0.5 ml back in. |</p>
<table>
<thead>
<tr>
<th>Blanks:</th>
<th>Add 0.5 ml of deionized water to the blank test tubes.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standards:</td>
<td>Start with 1000 ppm stock solutions of Al, Si, and Fe, and possibly the ion chromatograph elements too. Add 0.2 ml of each of these and put them into a 100 ml volumetric flask. The element concentration is 2 ppm. Put 0.5 ml of this into the standard test tubes.</td>
</tr>
<tr>
<td>Diluting solution:</td>
<td>Make a diluting solution of 1 liter of water and 10 microliters of 1000 ppm cobalt stock solution. This yields 10 ppb Co. Add 9.5 ml of this to the unknown, blank, and standard test tubes. Unknowns have a dilution factor of 20, standards have 0.1 ppm of all elements, and Co is the internal standard (Co has a low intrinsic background and works well in different analytical modes; it seems to be stable in DI water solution for at least days).</td>
</tr>
</tbody>
</table>