ESS 312 Geochemistry - Water-rock reactions

Constructing a phase diagram for feldspar weathering

Below is a list of aluminosilicate minerals formed from weathering of K-feldspar. Note that many of the minerals formed in the real-world weathering environment have complicated structures and compositions. The phases listed below are simple analogs for these minerals. Remember also that most of the thermodynamic data listed below are estimated or derived "empirically" - in other words, the various equilibrium constants are juggled until predicted mineral stabilities match geological observations.

K - feldspar: KAlSi3 O8 weathers to form ...

Gibbsite : Al (OH)₃

Kaolinite: $Al_2 Si_2 O_5 (OH)_4$

Muscovite (an analog of illite, but with a better defined composition): $KAl_2 Si_3 AlO_{10} (OH)_2$

Pyrophyllite : Al₂ Si₄ O₁₀ (OH)₂

The weathering reactions that occur when K – feldspar comes into contact with rainwater, river water or soil moisture generally consume H^+ and release dissolved K^+ to solution. Aqueous silica, (which we can write as SiO₂ even though the dissolved species is more correctly described as the hydrated neutral complex H₄ SiO₄)

is a participant in many reactions. Aluminum is found at very low concentrations in most natural waters. For these reasons, it is logical to choose to describe the weathering process in terms of reactions that :

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(i) Keep Al in the solid phases rather than liberate dissolved Al^{3+} ,

which is not observed. This is referred to as ' conserving Al to the solid phases'.

(ii) Consume or release K⁺ relative to H⁺ and consume or release SiO₂. Changes in the fluid phase

composition that take place during weathering can be described most easily in terms of the activity ratio $\left(\frac{a_{K^+}}{a_{H^+}}\right)$ and the silica activity a_{SiO_2} . We can plot the fluid composition on a diagram with axes $\log_{10}\left(\frac{a_{K^+}}{a_{H^+}}\right)$ and $\log_{10}\left(a_{SiO_2}\right)$.

Example 1 - Weathering of K-feldspar to kaolinite

Consider the reaction:

 $K - feldspar + H^+ + H_2 O \rightleftharpoons kaolinite + K^+ + SiO_{2(aq)}$... Now balance it :

 $2 \text{ KAlSi}_3 \text{ O}_8 + 2 \text{ H}^+ + \text{H}_2 \text{ O} \ \rightleftharpoons \ \text{Al}_2 \text{ Si}_2 \text{ O}_5 (\text{OH})_4 + 2 \text{ K}^+ + 4 \text{ SiO}_{2 \text{ (aq)}}$

... and write the expression for
$$K_{eq} = \frac{(a_{K^+})^2 (a_{SiO_2(aq)})^4}{(a_{H^+})^2} = 10^{-1.8}$$
.

Taking the log of both sides (be sure you see how and why we do this), gives:

$$\log_{10}\left(\frac{a_{K^{+}}}{a_{H^{+}}}\right) = -0.9 - 2\log_{10}\left(a_{SiO_{2(aq)}}\right)$$

This is the equation of a straight line, with slope -2 and intercept -0.9 in our $log\left(\frac{a_{K^+}}{a_{H^+}}\right)$ vs a_{SiO_2} diagram. The line represents the narrow range of K⁺,

 H^+ and dissolved SiO₂ activities at which K – feldspar and kaolinite can coexist. Either side of this line the K⁺,

 H^+ and SiO₂ activities favor the stability of one mineral over the other. To the right (high $a_{SiO_{2(aq)}}$),

K – feldspar is stable. To the left (lower $a_{SiO_{2}(aq)}$), kaolinite is the stable phase.

Example 2 - weathering of K-feldspar to 'muscovite'

Similarly, for the reaction:

 $K-feldspar + H^+ \rightleftharpoons muscovite + K^+ + SiO_{2(aq)}$,

which we can balance by ensuring Al is conserved between the solid minerals :

$$3 \text{ KAlSi}_3 \text{ O}_8 + 2 \text{ H}^+ \rightleftharpoons \text{ KAl}_2 \text{ Si}_3 \text{ Al } \text{O}_{10} (\text{OH})_2 + 2 \text{ K}^+ + 6 \text{ SiO}_{2 (\text{aq})}$$

... giving
$$K_{eq} = \frac{(a_{K^+})^2 (a_{SiO_2(aq)})^6}{(a_{H^+})^2} = 10^{-8.2}$$
.

Hence K-feldspar and muscovite can only be stable together at K+, H+ and dissolved SiO2 activities lying along the line

$$\log_{10}\left(\frac{a_{K^{+}}}{a_{H^{+}}}\right) = -4.1 - 3\log_{10}\left(a_{SiO_{2}}\right)$$

Again, high $a_{SiO_{2(aq)}}$ favors K – feldspar, low silica activity favors muscovite.

Example 3 - the reaction between kaolinite and 'muscovite'.

What conditions favor kaolinite over muscovite, or vice versa? Again, write a transformation reaction involving the two minerals and determine its slope $2 \text{ KAl}_2 \text{ Si}_3 \text{ Al } \text{O}_{10} (\text{OH})_2 + 2 \text{ H}^+ + 3 \text{ H}_2 \text{ O} \Rightarrow 3 \text{ Al}_2 \text{ Si}_2 \text{ O}_5 (\text{OH})_4 + 2 \text{ K}^+$

Notice that silica does not appear as a product or reactant in this reaction. This should suggest to you what the slope of the phase boundary will be.

For the reaction above $K_{eq} = \frac{(a_{K^+})^2}{(a_{H^+})^2} = 10^{11.0}$,

Hence kaolinite reacts with water to form muscovite across a phase boundary given by the line

$$\log_{10}\left(\frac{a_{K^+}}{a_{H^+}}\right) = 5.5$$
, with slope zero.

Use these examples to help you complete this week's lab, in which you're asked to write and balance similar reactions between gibbsite, K-feldspar, kaolinite, muscovite and quartz. Notice also that even when you're not given a value for K_{eq} of a reaction (and therefore can't figure out the intercept of the phase boundary) you can still determine its slope from the reaction stoichiometry.