Chemical weathering reactions

The mineral assemblage formed during the weathering process depends upon three factors:

- The mineralogical and textural composition of the parent rock.
- The composition and temperature of the aqueous solutions.
- The fluid flow (*i.e.*, rate of water flow and pore network)

Water composition and flow rate (*i.e.*, Rates of reaction)

The formation of minerals in the weathering environment is primarily the result of reaction between protons (i.e, H^+ in ground waters) and primary silicate minerals. Also important are reactions involving electron transfer (i.e., redox reactions).

Although the primary source of protons is a result of the production of organic acids in soil (not the absorption of atmospheric CO_2 by rain water) the production of acids can be viewed as the production of carbonic acid. This is because organic acids in surface soils readily oxidize to carbon dioxide. The oxidation of oxalic acid is shown below.

$$4\ HO_2CC_2O_2H + 2O_2 \dashrightarrow 8CO_2 + 4H_2O$$

Recalling that carbonic acid forms by the reaction,

$$H_2O + CO_2 \dashrightarrow H_2CO_3$$

At most soil pH conditions the carbonic acid immediately dissociates to bicarbonate and protons.

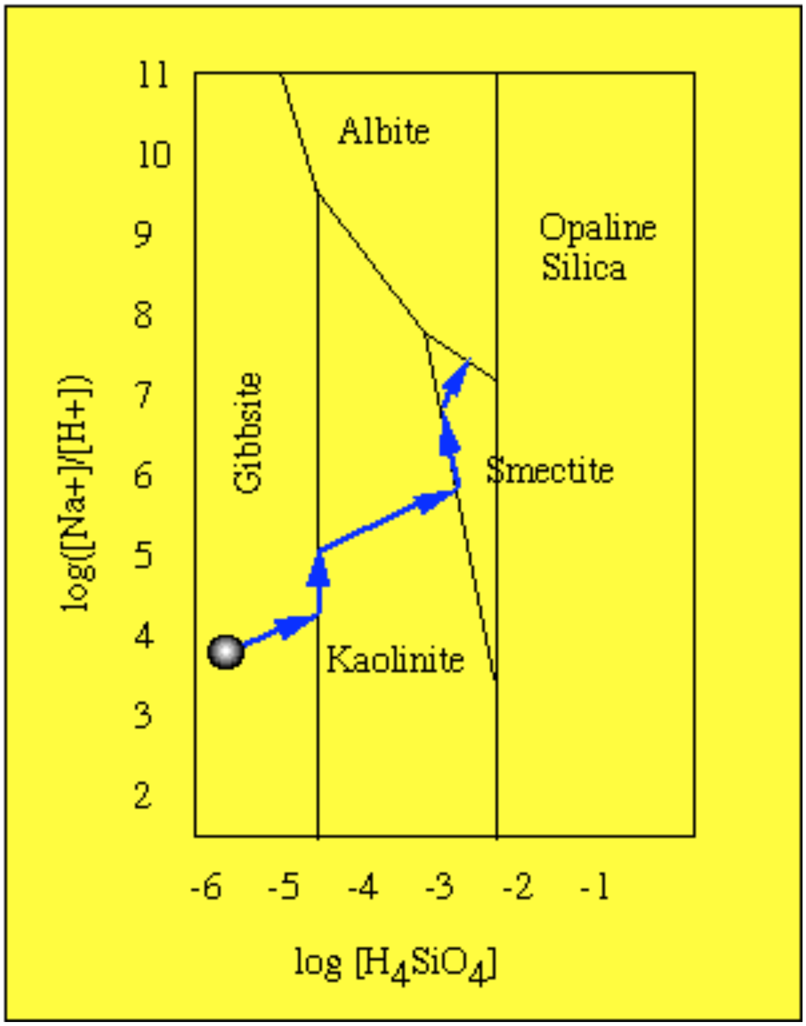
$$H_2CO_3 \dashrightarrow HCO_3^- + H^+$$

Example 1.

A typical weathering reaction in dilute waters with high acidity can be represented by reaction with ablite,

$$7\ H_2O + H^+ + NaAlSi_3O_8 \dashrightarrow Al(OH)_3 + Na^+ + 3\ H_4SiO_4^o$$

The stability fields for gibbsite, kaolinite, idealized smectite (Na-beidellite) and end-member albite are considered in the diagram below. Unlike our previous example, where we fixed the concentration of dissolved silica by quartz saturation, in this example the amount of dissolved H^+, Na^+, $H_4SiO_4^o$ and are allowed to vary. Recalling that Gibb's phase rule requires us to limit the degrees of freedom in our system, temperature and pressure must remain constant for the construction of a stability diagram that allow us to vary dissolved species. Recall also that the activity of solids and water are unity. The diagram below depicts concentrations in brackets, which indicates moles per liter. By doing so this allows us to use the stoichiometry of the reactions to determine how much the solution composition changes as reactions proceed. Also in this example, we will consider the situation where there is an excess of albite in the system.



1. If the water and reaction products do not leave the system (*i.e.*, very slow hydrologic flow rates) then the concentration of orthosilisic acid (i.e., dissolved silica) and the ratio of sodium to acid increase with time.

2. With time, the solution composition "evolves" and moves toward the NE part of the diagram. The slope of the trajectory is determined by the ratio of dissolved species produced and consumed. In the example above, for every H^+ that is consumed, there are 1 Na^+ and 3 $H_4SiO_4^o$ are produced. The slope of the trajectory is then $^1/_3$.

3. When the gibbsite - kaolinite boundary is encountered the gibbsite and excess $H_4SiO_4^o$ combine to form kaolinite. Na^+ is still being produced and H^+ is still being consumed. But the overall reaction silica is being incorporated into the kaolinite.

$$9\ H_2O + 2H^+ + 2NaAlSi_3O_8 \text{--->} Al_2Si_2O_5(OH)_4 + 2Na^+ + 4\ H_4SiO_4^o$$

$$-\quad 14\ H_2O + 2H^+ + 2NaAlSi_3O_8 \text{--->} 2Al(OH)_3 + 2Na^+ + 6\ H_4SiO_4^o$$

$$=\quad 2Al(OH)_3 + 2H_4SiO_4^o \text{--->} Al_2Si_2O_5(OH)_4 + 5H_2O \qquad \text{(overall reaction)}$$

4. As silica is released by dissolution of albite and it is used to make kaolinite, note that the $H_4SiO_4^o$ concentration does not change. The composition of the fluid evolves vertically, towards the north end of the diagram. Note that the kaolinite is a “less hydrous” than the gibbsite.

5. Once all the gibbsite is consumed, the fluid composition then evolves towards the NE again.

6. At the smectite - kaolinite boundary, both $H_4SiO_4^o$ and Na are used to form smectite. The fluid composition tracks along the kaolinite - smectite boundary until all the kaolinite is gone.

$$6.4\ H_2O + 2H^+ + 2.3NaAlSi_3O_8 \text{--->} Na_{0.3}Al_{2.3}Si_{3.7}O_{10}(OH)_2 + 2\ Na^+ + 3.2H_4SiO_4^o$$

$$-\quad 10.35\ H_2O + 2.3H^+ + 2.3NaAlSi_3O_8 \text{--->} Al_2Si_2O_5(OH)_4 + 2.3Na^+ + 4.6\ H_4SiO_4^o$$

$$=\quad 1.15Al_2Si_2O_5(OH)_4 + 0.3H^+ + 0.3Na^+ + 1.4H_4SiO_4^o \text{--->} Na_{0.3}Al_{2.3}Si_{3.7}O_{10}(OH)_2 + 3.95H_2O$$

7. Again, the fluid composition tracks to the NE until the albite-smectite uni-variant line is reached and equilibrium is achieved (i.e., rate of forward and reverse reactions are equal).

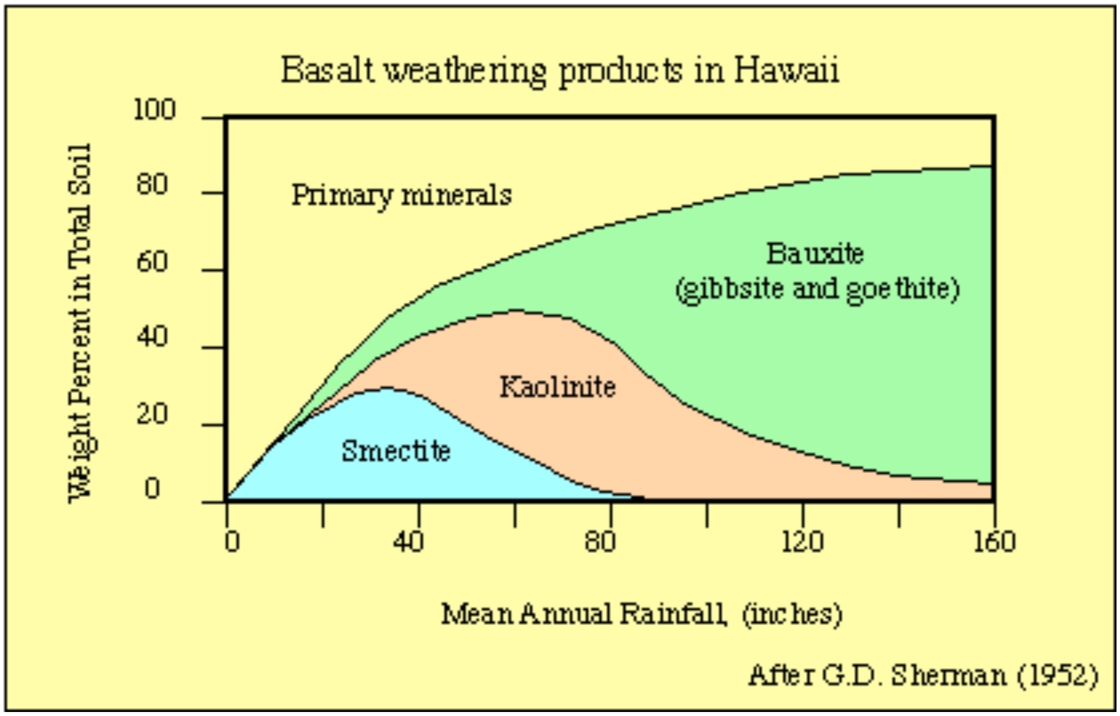
$$1.15Al_2Si_2O_5(OH)_4 + 0.3H^+ + 0.3Na^+ + 1.4H_4SiO_4^o \text{<--->} Na_{0.3}Al_{2.3}Si_{3.7}O_{10}(OH)_2 + 3.95H_2O$$

Example 2. Basalt weathering in Hawaii

The above scenario is for a closed system. Soils are open systems.

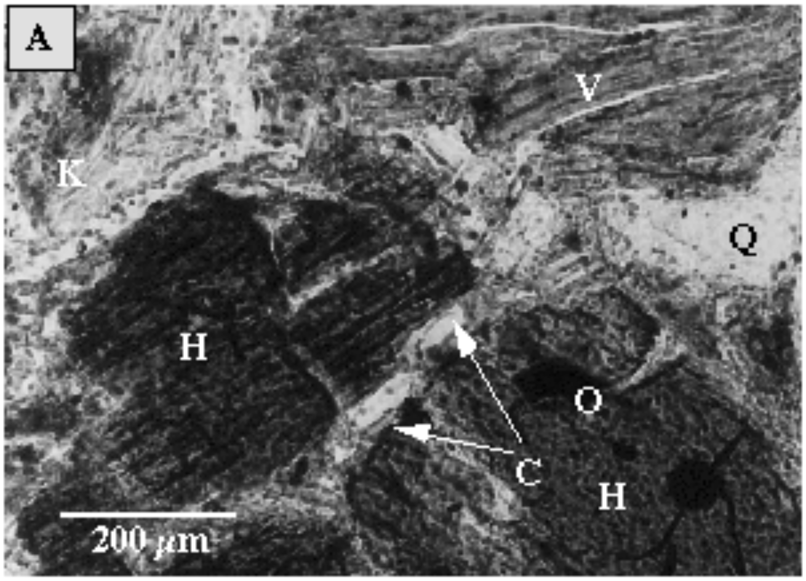
The faster the hydrodynamic flow rate, the shorter the contact time of solution with the primary minerals.
Soils developed in Hawaii display the effect of different weathering products from a parent (basalt).

The diagram below shows the effect of rainfall versus the percentage of clay minerals formed in soils.



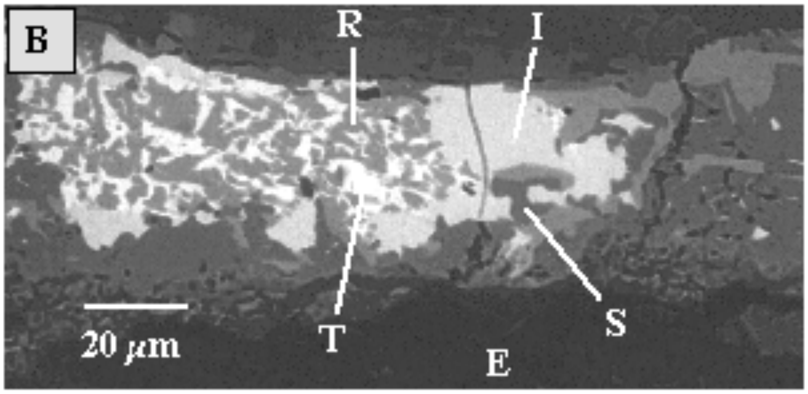
Example 3 Daniel Springs, GA metagabbro weathering

C-horizon changes

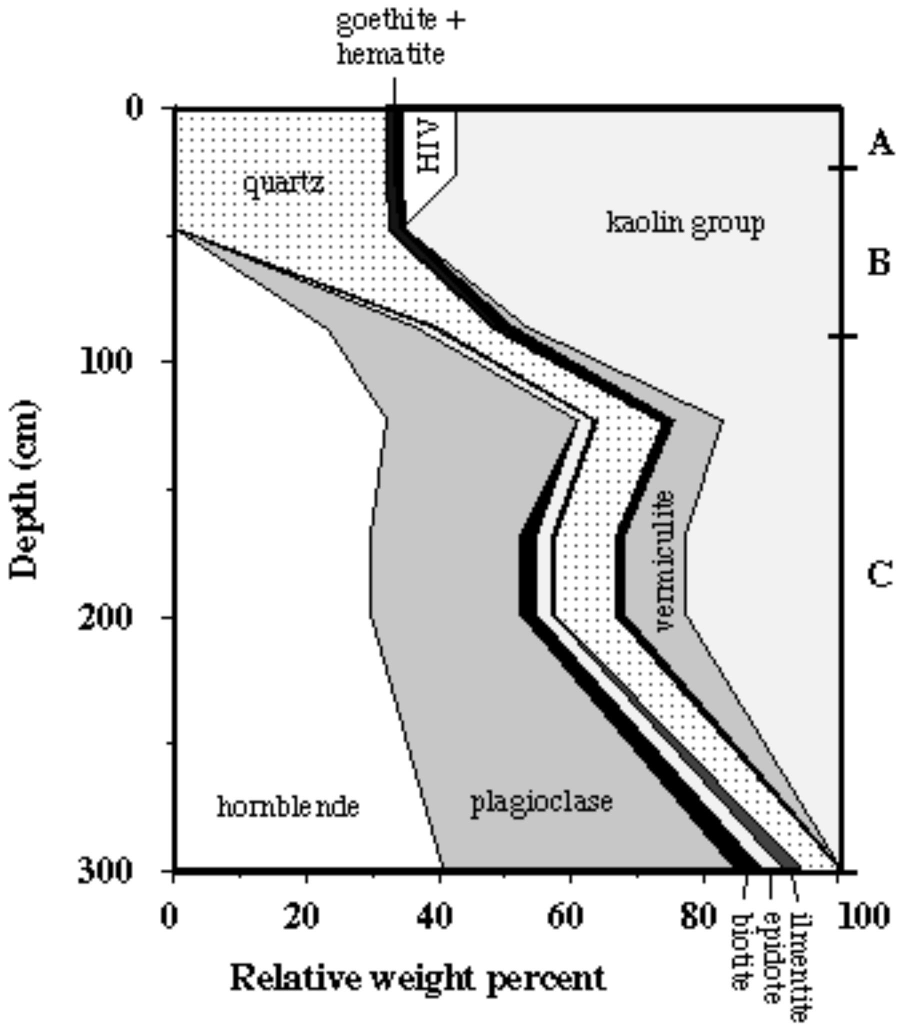


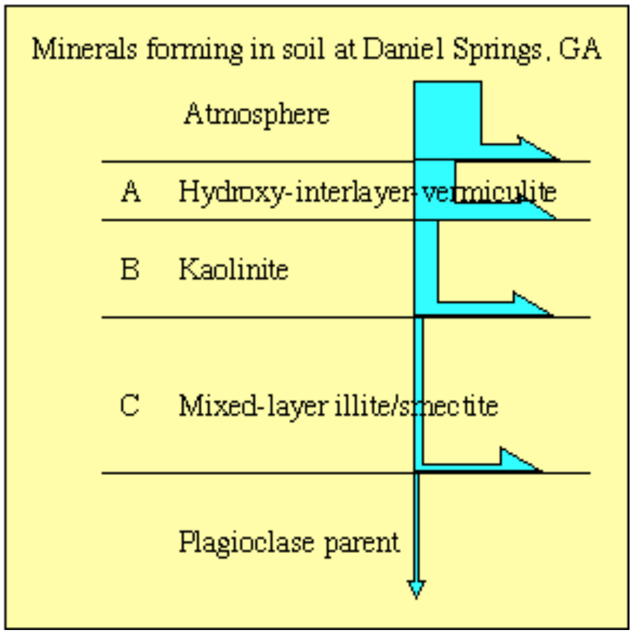
H = hornblende, K = kaolinite, C = clay, Q = quartz, O = opaque

Oxidation of ilmenite ($FeTiO_3$)



R = rutile, T = titanomagnetite, I = ilmenite, S = sphene, E = epoxy


goethite +
hematite
0
100
200
300
Depth (cm)
A
B
C
HIV
quartz
kaolin group
vermiculite
hornblende
plagioclase
0
20
40
60
80
100
Relative weight percent
biotite
epidote
ilmenite


Minerals forming in soil at Daniel Springs, GA
Atmosphere
A Hydroxy-interlayer vermiculite
B Kaolinite
C Mixed-layer illite/smectite
Plagioclase parent