Weathering Process

Because most rock forming minerals were formed under high temperature and high pressure conditions, they are not stable at low temperatures and pressures which exist at the earth’s surface, especially in the presence of H₂O, O₂, CO₂ and microorganisms. That’s why weathering takes place. Weathering is a process in which rock minerals (or primary minerals) are transformed into soil minerals (or secondary minerals). In general, the rate of weathering is a function of:

\[
\frac{\Delta \text{weathering}}{\Delta \text{time}} = f (\text{climate, topography, parent material and biosphere})
\]

For example, the weathering is faster in warm and wet climates than in cold and dry climates; it’s faster on steep slopes than on flat area; limestone is weathered faster than granite; weathering is faster under strong microbial activities. And because of this weathering process, soils are transformed and have different properties at different stages of weathering. For example:

![Fig. 3.1 Schematic progression of basic and acidic zones through soils during soil development. This sequence also represents soil profiles from arid to humid to humid tropical regions.](image-url)
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Chemical processes of mineral formation in soils

a.) Feldspar $\rightarrow$ Kaolinite

The formation of secondary minerals in soils generally results from the recombination and addition of ions and molecules from the soil solution to the solid phase. This process is slow but does happen.

Ex: the weathering of feldspar to form kaolinite.

First feldspar dissolves under acid conditions

$$\text{NaAlSi}_3\text{O}_8 + 4\text{H}_2\text{O} + 4\text{H}^+ \rightarrow \text{Na}^+ + \text{Al}^{3+} + 3\text{Si(OH)}_4$$

Albite (Na feldspar) soluble silica

Next soil solution Al$^{3+}$ will react with soluble silica to form kaolinite:

$$\text{Al}^{3+} + \text{Si(OH)}_4 + \frac{1}{2}\text{H}_2\text{O} \rightarrow 3\text{H}^+ + \frac{1}{2}\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$$

Kaolinite

Sometimes, the two reactions are combined into an overall reaction to show feldspar as the reactant and kaolinite as the direct product:

$$\text{NaAlSi}_3\text{O}_8 + 4\frac{1}{2}\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{Na}^+ + 2\text{Si(OH)}_4 + \frac{1}{2}\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$$

Albite Kaolinite

During the weathering process, Na$^+$ and soluble silica are released into soil solution, which may move down the soil profile by leaching. There they can react with other ions or molecules to form other minerals or finally be lost to the sea.

If you notice here, the ratio of Si:Al in feldspar is 3:1. The weathering process usually reduces this ratio to about 1:1. That means some silica is always lost in the weathering process.

b.) Kaolinite $\rightarrow$ Gibbsite

Kaolinite, in turn, will eventually weather to gibbsite.
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\[ \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 5\text{H}_2\text{O} \rightarrow \leftrightarrow 2\text{Al}(\text{OH})_3 + 2\text{Si}(\text{OH})_4 \]

<table>
<thead>
<tr>
<th>Kaolinite</th>
<th>Gibbsite</th>
<th>Soluble silica</th>
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The activities of solids and of water are assumed to be unity. The equilibrium between the two minerals is therefore determined by the activity of the only soluble species, \( \text{Si(OH)}_4 \)

\[
k = (\text{Si(OH)}_4)^2 = 10^{-9} \\
\text{Si(OH)}_4 = 10^{-4.5} \text{ M}
\]

If activity of \( \text{Si(OH)}_4 < 10^{-4.5} \text{ M} \) then…
- Gibbsite is stable
- Kaolinite will not form
- If any kaolinite has been present, it will decompose to gibbsite and soluble silica.

On the other hand, if \( \text{Si(OH)}_4 > 10^{-4.5} \text{ M} \) then kaolinite is stable,
- gibbsite is unstable; that is, it will not form or if it has been there, it will react with \( \text{Si(OH)}_4 \) to form kaolinite.

c.) Acid saturation and dissolution of montmorillonite

If montmorillonite (or smectite, in general) is saturated with \( \text{H}^+ \), it will self decompose. Protons will react with \( \text{Al} \) in the clay structure, the clay collapses and \( \text{Al} \) becomes exchangeable.

\[ \text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2 + 6\text{H}^+ + 4\text{H}_2\text{O} \leftrightarrow 2\text{Al}^{3+} + 4\text{Si(OH)}_4 \]

As far as weathering is concerned, the order of stability of these soil minerals is as follows:

vermiculite < montmorillonite < kaolinite < gibbsite < hematite

least stable most stable
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It means that montmorillonite, when weathered, will form kaolinite; and kaolinite when weathered, will form gibbsite.

d.) Soil carbonates

In regions of limited rainfall where evapo-transpiration is greater than infiltration rate, CaCO₃ is likely to accumulate. The chemical reaction responsible for this process is:

\[ \text{Ca}^{2+} + \text{H}_2\text{O} + \text{CO}_2 \leftrightarrow \text{CaCO}_3 + 2\text{H}^+ \] (1)

Alkaline conditions favor CaCO₃ accumulation, by consuming H⁺ and driving the reaction to the right. In acid soils, CaCO₃ dissolves; equation (1) goes to the left. Increasing partial pressure of CO₂ in soil air (P_{CO₂}) causes CaCO₃ to react further:

\[ \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- \] (2)

What it means is that CaCO₃ re-dissolves with increasing CO₂ concentration in the gaseous phase. However, in soils with relatively high concentrations of Ca⁺ and limited water content, reaction (1) is favored and reaction (2) is suppressed.

When CaCO₃ is present in soils at high concentrations, say several percent, then it controls both soil pH and soil solution Ca²⁺ as shown below.

\[ \text{CaCO}_3 (s) \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-} \]

\[ \text{ksp} = (\text{Ca}^{2+})(\text{CO}_3^{2-}) = 10^{-8.4} \] (3)

- **Carbonate species in soil solution**

CO₂ dissolves in water to form a weak acid, H₂CO₃.

\[ \text{CO}_2 (g) + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 (\text{aq}) \text{ or H}_2\text{CO}_3 \]

The solubility of CO₂ and other gases is governed by Henry’s law, which relates the partial pressure of a gas to its concentration in solution.
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\[ K_H = \frac{(H_2CO_3)}{P_{CO_2}} = 10^{-1.5} \quad (4) \]

H₂CO₃, however, doesn’t stay as it is, but it dissociates into HCO₃⁻ and CO₃²⁻ ions as the pH increases.

\[ H_2CO_3 \rightarrow H^+ + HCO_3^- \quad (5) \]

\[ K_1 = \frac{(H^+)(HCO_3^-)}{(H_2CO_3)} = 10^{-6.4} \quad \text{pK}_1 = 6.4 \]

\[ HCO_3^- \rightarrow H^+ + CO_3^{2-} \quad (6) \]

\[ K_2 = \frac{(H^+)(CO_3^{2-})}{(HCO_3^-)} = 10^{-10.3} \quad \text{pK}_2 = 10.3 \]

The concentrations of various ions can be calculated from these equations by assuming a value for P_{CO₂}.

For example:

From eq. (4)
\[ H_2CO_3 = 10^{-1.5} P_{CO_2} \]

eq. (5) gives:
\[ (HCO_3^-) = 10^{-6.4} \times \frac{(H_2CO_3)}{(H^+)} = 10^{-6.4} \times \frac{(10^{-1.5})}{(H^+)} \]
\[ (HCO_3^-) = 10^{-7.9} \frac{P_{CO_2}}{(H^+)} \]

eq. (6) gives:
\[ CO_3^{2-} = 10^{-10.3} \times \frac{(HCO_3^-)}{(H^+)} \]
\[ = (CO_3^{2-}) = 10^{-18.2} \times \frac{P_{CO_2}}{(H^+)^2} \]

From these equations, acidity of rain water can be calculated by assuming that rain is in equilibrium with CO₂ of the atmosphere (P_{CO₂} = 0.00038). pH of such water would be around 5.6-5.7.