

Chapter 5

Geochemical Weathering

Weathering of landscapes involves an array of mechanical and geochemical agents that conspire to alter primary geological formations to sediments and solutes. Geochemical weathering is driven by water. In soils, water is the limiting factor for the activity of aerobic bacteria that degrade organics and produce CO₂ at partial pressures orders of magnitude higher than in the atmosphere. Soil CO₂ is hydrated by soil water, providing carbonic acid for the dissolution of primary carbonate and silicate minerals. Water also hosts the bacterial oxidation of sulfides, ferrous iron and other redox reactions in the weathering of minerals. Finally, it is water, with its polar character and capacity to hydrate and hydroxylate that facilitates dissolution of primary mineral phases and transport of solutes in groundwater.

Primary phases include high temperature minerals formed by magmatic and metamorphic processes — the aluminosilicate granites and gneisses that make up shield terrains of continental cratons, and ferromagnesian silicates like basalts that dominate in volcanic belts. The kinetics of silicate weathering are slow, with the formation of secondary clays — hydrated aluminosilicate minerals with high capacity for cation exchange and sorption. Weathering of carbonate rocks proceeds more rapidly than weathering of silicate rocks. These are dissolution reactions, generating porosity and accelerating water movement. Carbonate minerals are ubiquitous, not just as limestone and dolomite formations, but as secondary phases filling fractures in silicate rocks, and as cements and crusts in soils.

In near-surface environments found in unsaturated soils and fractures, CO₂ and O₂ consumed by reaction are continually replenished by diffusion into water from the soil air or open atmosphere. Here, weathering proceeds with unrestricted access to these essential reactants under *open system conditions*. In the saturated zone below the water table, acidity and oxygen are limited to the concentrations dissolved during recharge. Here weathering proceeds under *closed system conditions*. Closed system conditions exist in recharge areas characterized by rapid infiltration and percolation to the water table. Conditions evolve rapidly towards high pH values and reduced reaction. By contrast, weathering is more aggressive under open system conditions, resulting in higher concentrations of solutes, and is increased with residence time for water in unsaturated soils.

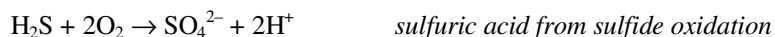
This chapter explores the geochemical evolution of groundwater — the mineralization of groundwater by geochemical weathering, and the evolution of DIC and pH. Both open and closed systems are explored for carbonate and silicate terrains.

Weathering reactions and the consumption of acidity

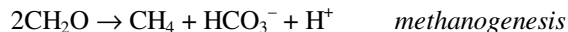
The primary aqueous reactions in groundwater systems that produce acidity involve atmospheric oxygen and some reduced compound such as organic carbon. Bacterially-mediated respiration is the most important. Respiration takes place mainly in soil water within the unsaturated zone of organic-rich soils where abundant oxygen is available.



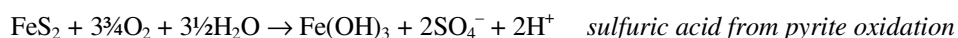
Degradation of organics also releases organic sulfur and nitrogen, both of which are generally found in fixed or reduced states in organic compounds. Mineralization of these elements to compounds like sulfide [H₂S] and ammonia [NH₄⁺] makes them available for oxidation in aerobic reactions generally mediated by bacteria.



Production of these reduced compounds is favored in highly-reducing organic-rich environments such as lake and marine sediments, wetlands, wastewater ponds, septic systems and landfill leachates. Reducing environments like these also produce methane through bacterial degradation of organic carbon. While there is a consortium of intermediary reactions involving fatty acids like acetate [CH_3COOH] and hydrogen gas [H_2], the overall reaction produces carbonic acid. These are circum-neutral pH reactions and so carbonic acid dissociates into bicarbonate and hydrogen ions. Thus, buried organics in sedimentary aquifers can be a significant source of acidity in groundwaters:



Bedrock is also a source of reduced compounds that release acidity through oxidation. Sulfide minerals such as pyrite are ubiquitous in parent materials including shales, limestones and igneous rocks, and can be a component of unconsolidated tills. Other base metal sulfides are less commonly present. As soils develop, these minerals become exposed and are oxidized by bacteria. Ferrous iron [Fe^{2+}] present in pyrite as well as in a host of ferromagnesian silicates like olivine [Fe_2SiO_4] and pyroxene [FeSi_2O_5] is released by weathering, and provides an additional source of acidity through oxidation. Precipitation of ferric iron hydroxide [$\text{Fe}(\text{OH})_3$] in soils and on outcrops is evidence for this source of acidity.

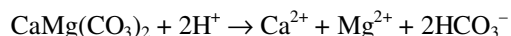
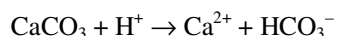


Finally, the process of biodegradation in soils is accompanied by the production of organic acids. Low molecular weight fatty acids such as acetate [CH_3COOH] are important intermediary compounds. These, however, can be rapidly consumed by aerobic bacteria and converted to CO_2 . The final organic products of biodegradation include the high molecular weight humic and fulvic acids — refractory compounds that make up most of the dissolved organic carbon (DOC) in groundwaters. These organic acids dissociate in the pH 2 to 4 range, and so provide an additional source of H^+ for weathering.

The production of acidity in groundwater by these reactions is reflected by the concentration of the anion products, provided that contributions of these anions from the bedrock can be accounted for. Sulfate, for example, can be a measure of the acidity generated by pyrite or organic sulfur oxidation, providing contributions from gypsum dissolution or seawater mixing can be established. Carbonate alkalinity, alk_C , is more problematic given that calcite weathering can contribute up to half of the carbonate alkalinity in water. However, in silicate terrains where calcite is not present, alk_C can be a measure of mineral weathering.

WEATHERING IN CARBONATE TERRAINS

Carbonate bedrock — limestone and dolomite, underlies a significant percentage of the Earth's land surface. Carbonate aquifers are common and figure highly in the supply of groundwater to wells and to surface water bodies. Much of the geochemistry of groundwater and surface waters is established by the weathering of carbonate terrain. Even in silicate terrains, such as metamorphic and igneous bedrock, carbonate minerals can be present as fracture fillings. Despite a low relative abundance, their higher rate of weathering allows that carbonates have the dominant effect on watershed geochemistry. Two principal reactions dominate — calcite and dolomite dissolution.



Open system carbonate weathering

Much of carbonate weathering occurs under open system conditions, where the reservoir of soil CO_2 and organics replenish the acidity consumed by mineral dissolution. Contact with soil CO_2 also maintains a

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constant P_{CO_2} and restrains pH to the circum-neutral range. As shown in the next section, this contrasts with carbonate dissolution under closed system conditions where the limited CO_2 gained during infiltration through the soil precludes extensive weathering. Here, the P_{CO_2} will evolve to very low values with correspondingly high pH.

The low P_{CO_2} of the atmosphere and ephemeral character of runoff waters does not allow significant surface weathering of carbonates. As precipitation infiltrates through unsaturated soils or unsaturated fractured bedrock, the much higher subsurface P_{CO_2} and production of organic acids drives mineral weathering, with associated increases in DIC, pH and Ca^{2+} .

The relatively high solubility of calcite and its contribution to DIC makes carbonate weathering an important process in the evolution of groundwater quality. Contributions from limestone terrains are important, as are calcite fracture fillings in silicate terrains. In all cases, the degree of carbonate weathering is largely determined by the availability of CO_2 and limited by the saturation of calcite. In carbonate terrains, infiltrating waters often achieve calcite saturation within the unsaturated soil zone under open system conditions. The amount of carbonate dissolved is ultimately controlled by partial pressure of CO_2 of the system. The concentration of Ca^{2+} as well as the DIC and pH of the groundwater can be easily calculated using the basic equations that control DIC speciation presented in the previous chapter. It is also a useful exercise for understanding the importance of open system weathering.

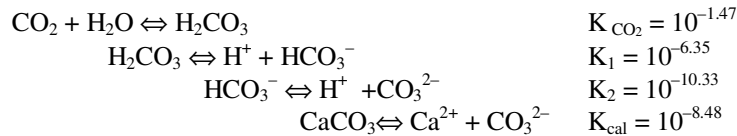
Example 5-1 Carbonate dissolution under open system conditions

How much calcite can be dissolved by water in an open system with P_{CO_2} of $10^{-1.5}$ at 25°C ?

Under open system conditions, the carbonic acid activity, remains constant under conditions of fixed P_{CO_2} :

$$\begin{aligned} K_{\text{CO}_2} &= \frac{a_{\text{H}_2\text{CO}_3}}{P_{\text{CO}_2}} = 10^{-1.47} \\ a_{\text{H}_2\text{CO}_3} &= K_{\text{CO}_2} \cdot P_{\text{CO}_2} \\ &= 10^{-1.47} \cdot 10^{-1.5} \\ &= 10^{-2.97} \end{aligned}$$

Carbonic acid dissociates to give equal concentrations of HCO_3^- and H^+ (Example 4-6). However, as calcite begins to dissolve, CO_3^{2-} is converted to HCO_3^- by reaction with H^+ . This causes more H_2CO_3 to dissociate and more CO_2 to diffuse into solution. The relevant reactions, at the point of calcite saturation, include:



Under open system conditions, the fixed parameters include only $P_{\text{CO}_2} = 10^{-1.5}$ atm, and $a_{\text{H}_2\text{CO}_3} = 10^{-2.97}$. Unknown parameters include H^+ , HCO_3^- , CO_3^{2-} and Ca^{2+} – which is the amount of calcite dissolved. Solving for these unknowns begins with the basic equations for DIC speciation and calcite dissolution (Chapter 3; Table 3-2). By substitution and rearrangement, they can be expressed in terms of a_{H^+} (pH):

$$a_{\text{HCO}_3^-} = \frac{K_1 \cdot a_{\text{H}_2\text{CO}_3}}{a_{\text{H}^+}} = \frac{10^{-6.35} \cdot 10^{-2.97}}{a_{\text{H}^+}} = \frac{10^{-9.32}}{a_{\text{H}^+}}$$

$$a_{\text{CO}_3^{2-}} = \frac{K_2 \cdot a_{\text{HCO}_3^-}}{a_{\text{H}^+}} = \frac{10^{-10.33} \cdot 10^{-9.32}}{a_{\text{H}^+}} = \frac{10^{-19.65}}{a_{\text{H}^+}^2}$$

$$a_{\text{Ca}^{2+}} = \frac{K_{\text{calcite}}}{a_{\text{CO}_3^{2-}}} = \frac{10^{-8.48}}{10^{-19.65} / a_{\text{H}^+}^2} = 10^{11.17} \cdot a_{\text{H}^+}^2$$

A fourth equation is required to solve for four unknown parameters. Since the solution must be electrically neutral, we can use the charge balance equation:

$$2m_{\text{Ca}^{2+}} + m_{\text{H}^+} = m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{OH}^-}$$

Considering that for circum-neutral systems like this, H^+ , OH^- , and CO_3^{2-} will have very low concentrations compared to Ca^{2+} and HCO_3^- (as demonstrated by the equation for calcite dissolution — $\text{CaCO}_3 + \text{H}_2\text{CO}_3 = \text{Ca}^{2+} + 2\text{HCO}_3^-$) the charge balance equation can be simplified to:

$$2m_{\text{Ca}^{2+}} = m_{\text{HCO}_3^-}$$

Substituting into the charge balance equation for $m_{\text{Ca}^{2+}}$ and $m_{\text{HCO}_3^-}$ solves for H^+ :

$$2 \times 10^{11.17} \cdot a_{\text{H}^+}^2 = \frac{10^{-9.32}}{a_{\text{H}^+}}$$

$$10^{-3\text{pH}} = 10^{-20.79}$$

$$\text{pH} = 6.93$$

With pH, all other components can be solved. This gives a Ca^{2+} concentration of:

$$m_{\text{Ca}^{2+}} = 10^{11.17} \cdot a_{\text{H}^+}^2 = 10^{11.17} \cdot 10^{-13.86} = 10^{-2.69} = 0.00204 \text{ mol/kg}$$

$$= 81.8 \text{ ppm}$$

Thus, $0.00204 \times 1000 \times 100$ ($\text{gfw}_{\text{calcite}}$) = 204 mg/L of calcite have been dissolved under open system conditions. If the P_{CO_2} is greater, say 10^{-1} (10% CO_2), the final pH is lower (6.60) and the amount of calcite dissolved increases to 295 mg/L.

Closed system carbonate weathering

Once groundwaters have infiltrated through the unsaturated zone and below the water table, the access to soil or atmospheric CO_2 is limited by the rate of diffusion through water. As this is effective for depths of a few centimeters at most, groundwaters within the saturated zone are essentially cut off from soil CO_2 , and weathering proceeds under closed system conditions. The degree of mineral weathering is then limited to the amount of CO_2 gained during recharge. As this is consumed, P_{CO_2} decreases, pH increases, and the rate of carbonate dissolution is diminished.

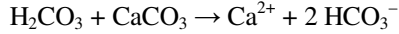
Calculating the dissolution of calcite under closed system conditions is more complicated than for open system conditions because the initial P_{CO_2} decreases as the system moves towards equilibrium. However, a unique solution exists for a given initial P_{CO_2} , and can be determined from the DIC reaction equations used above, plus equations of electroneutrality and mass balance.

How much calcite can be dissolved under closed system conditions with an initial P_{CO_2} of $10^{-1.5}$?

With this initial condition, the total DIC in the system before calcite dissolution can be calculated according to the equations used in Example 6-1. Again, it is acceptable to approximate molalities, m , from activities, a .

$$\begin{aligned} P_{\text{CO}_2} &= 10^{-1.5} \\ m_{\text{H}_2\text{CO}_3} &= P_{\text{CO}_2} \cdot K_{\text{CO}_2} = 10^{-1.47} \cdot 10^{-1.5} \\ &= 10^{-2.97} = 0.00107 \text{ mol/kg} \end{aligned}$$

This is the initial concentration of acid available for calcite dissolution according to the reaction:



Given that one mole of calcite is dissolved per mole of carbonic acid, a total dissolution of 1.07 mmol/kg or 107 ppm CaCO_3 can be predicted. More rigorous calculations bear this out, beginning with a calculation of the initial DIC concentration and pH:

$$\begin{aligned} K_1 &= \frac{a_{\text{HCO}_3^-} \cdot a_{\text{H}^+}}{a_{\text{H}_2\text{CO}_3}} \\ a_{\text{HCO}_3^-} \cdot a_{\text{H}^+} &= 10^{-6.35} \cdot 10^{-2.97} = 10^{-9.32} \\ a_{\text{HCO}_3^-} &= \sqrt{10^{-9.32}} = 10^{-4.66} = 0.000022 \text{ mmol/kg} \end{aligned}$$

As the dissociation of H_2CO_3 is an acidic reaction ($\text{pH} = 4.66$), CO_3^{2-} will have a minimal concentration, and so the initial DIC concentration will be:

$$\begin{aligned} m_{\text{DIC}} &= 0.00107 + 0.000022 \\ &= 0.00109 \text{ mol/kg} \end{aligned}$$

The final concentrations of H_2CO_3 , HCO_3^- , CO_3^{2-} , H^+ , OH^- and Ca^{2+} are not known. However, their relative concentrations are established by the following equations:

$$\begin{aligned} a_{\text{HCO}_3^-} &= \frac{K_1 \cdot a_{\text{H}_2\text{CO}_3}}{a_{\text{H}^+}} \approx \frac{10^{-6.35} \cdot m_{\text{H}_2\text{CO}_3}}{10^{-\text{pH}}} \\ a_{\text{CO}_3^{2-}} &= \frac{K_2 \cdot a_{\text{HCO}_3^-}}{a_{\text{H}^+}} \approx \frac{10^{-10.33} \cdot m_{\text{HCO}_3^-}}{10^{-\text{pH}}} \\ a_{\text{Ca}^{2+}} &= \frac{K_{\text{calcite}}}{a_{\text{CO}_3^{2-}}} \approx \frac{10^{-8.48}}{m_{\text{CO}_3^{2-}}} \\ a_{\text{OH}^-} &= \frac{K_{\text{H}_2\text{O}}}{a_{\text{H}^+}} = \frac{10^{-14}}{10^{-\text{pH}}} \end{aligned}$$

There are six unknown parameters and four equations. Two additional equations that can be used are the mass balance equation, where the amount of dissolved calcite ($m_{\text{Ca}^{2+}}$) is equal to the total DIC minus the initial DIC of 0.00109 mol/L:

$$\text{Mass balance equation: } m_{\text{Ca}^{2+}} = m_{\text{H}_2\text{CO}_3} + m_{\text{HCO}_3^-} + m_{\text{CO}_3^{2-}} - 0.00109$$

and the charge balance equation, based on the law of electroneutrality:

$$\text{Charge balance equation: } 2m_{\text{Ca}^{2+}} = m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{OH}^-} - m_{\text{H}^+}$$

As the solution at equilibrium will have high pH, we can simplify by assuming that $m_{\text{H}_2\text{CO}_3}$ and m_{H^+} will not be significant in these two equations. Then multiplying the simplified mass balance equation by two and equating it with the charge balance equation gives:

$$\text{Mass balance equation: } 2m_{\text{Ca}^{2+}} = 2m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} - 0.0022$$

$$\text{Charge balance equation: } 2m_{\text{Ca}^{2+}} = m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{OH}^-}$$

$$2m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} - 0.0022 = m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{OH}^-}$$

$$m_{\text{HCO}_3^-} = m_{\text{OH}^-} + 0.0022$$

Substitution into the equations above allows the components of the mass balance equation to all be expressed in terms of m_{H^+} :

$$\begin{aligned} m_{\text{HCO}_3^-} &= m_{\text{OH}^-} + 0.0022 \\ &= \frac{10^{-14}}{m_{\text{H}^+}} + 0.0022 \\ m_{\text{CO}_3^{2-}} &= \frac{10^{-10.33} \cdot m_{\text{HCO}_3^-}}{m_{\text{H}^+}} = \frac{10^{-10.33}}{m_{\text{H}^+}} \cdot \left(\frac{10^{-14}}{m_{\text{H}^+}} + 0.0022 \right) \\ m_{\text{Ca}^{2+}} &= \frac{10^{-8.48}}{m_{\text{CO}_3^{2-}}} = \frac{10^{-8.48}}{\frac{10^{-10.35}}{m_{\text{H}^+}} \cdot \left(\frac{10^{-14}}{m_{\text{H}^+}} + 0.0022 \right)} \end{aligned}$$

This provides a unique solution to the mass balance equation:

$$\frac{10^{-8.48}}{\frac{10^{-10.35}}{m_{\text{H}^+}} \cdot \left(\frac{10^{-14}}{m_{\text{H}^+}} + 0.0022 \right)} = \frac{10^{-14}}{m_{\text{H}^+}} + 0.0022 + \frac{10^{-10.35}}{m_{\text{H}^+}} \cdot \left(\frac{10^{-14}}{m_{\text{H}^+}} + 0.0022 \right) - 0.00109$$

which can be simplified:

$$\frac{10^{-8.48} \cdot m_{\text{H}^+}^2}{\left(\frac{10^{-24.35}}{m_{\text{H}^+}} + 10^{-13.01} \right)} = 10^{-14} + \left(\frac{10^{-24.35}}{m_{\text{H}^+}} + 10^{-13.01} \right) + 0.0011 \cdot m_{\text{H}^+}$$

$$\begin{aligned} 10^{-8.48} \cdot m_{\text{H}^+}^2 &= 10^{-14} \left(\frac{10^{-24.35}}{m_{\text{H}^+}} + 10^{-13.01} \right) + \left(\frac{10^{-24.35}}{m_{\text{H}^+}} + 10^{-13.01} \right)^2 + 0.0011 m_{\text{H}^+} \left(\frac{10^{-24.35}}{m_{\text{H}^+}} + 10^{-13.01} \right) \\ &= \left(\frac{10^{-38.35}}{m_{\text{H}^+}} + 10^{-27.01} \right) + \frac{10^{-48.7}}{m_{\text{H}^+}^2} + 2 \cdot \frac{10^{-37.36}}{m_{\text{H}^+}} + 10^{-26.02} + 10^{-27.31} + 10^{-15.96} m_{\text{H}^+} \end{aligned}$$

Multiplying through by $m_{\text{H}^+}^2$ and collecting terms renders a quadratic equation which is most easily solved by trial and error by using a goal seek function on a spreadsheet:

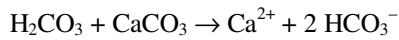
$$10^{-48.7} = 10^{-8.48} m_{\text{H}^+}^4 - 10^{-16.0} m_{\text{H}^+}^3 - 10^{-26.0} m_{\text{H}^+}^2 - 10^{-37.0} m_{\text{H}^+}$$

Accordingly, $m_{\text{H}^+} = 10^{-7.48}$

and $\text{pH} = 7.48$

$$\begin{aligned}
 m_{\text{HCO}_3^-} &= \frac{10^{-14}}{m_{\text{H}^+}} + 0.0022 \\
 &= \frac{10^{-14}}{10^{-7.48}} + 0.0022 = 0.0022 \text{ mol/kg} \\
 m_{\text{CO}_3^{2-}} &= \frac{10^{-10.35} \cdot 0.0022}{10^{-7.48}} = 2.97 \cdot 10^{-6} \text{ mol/kg} \\
 m_{\text{Ca}^{2+}} &= m_{\text{HCO}_3^-} + m_{\text{CO}_3^{2-}} - 0.00109 \\
 &= 0.0022 + 2.97 \cdot 10^{-6} - 0.00109 \\
 &= 0.0011
 \end{aligned}$$

Thus, only 0.0011 mol/kg or 110 ppm of calcite has been dissolved. Note that this amount is roughly the same as the initial concentration of carbonic acid (0.00107 mol/kg). This is due to the stoichiometry of the calcite dissolution equation:



This allows a considerable simplification to the problem. In effect, one mole of H_2CO_3 will dissolve 1 mole of CaCO_3 in a simple closed system setting.

In this case, the 110 mg/L of dissolved calcite is considerably less than the 295 mg/L that can be dissolved under open system conditions in Example 5-1, and underlines the importance of open system vs. closed system weathering on geochemical evolution. At lower initial P_{CO_2} , the greater weathering potential under open vs. closed system conditions becomes even more apparent.

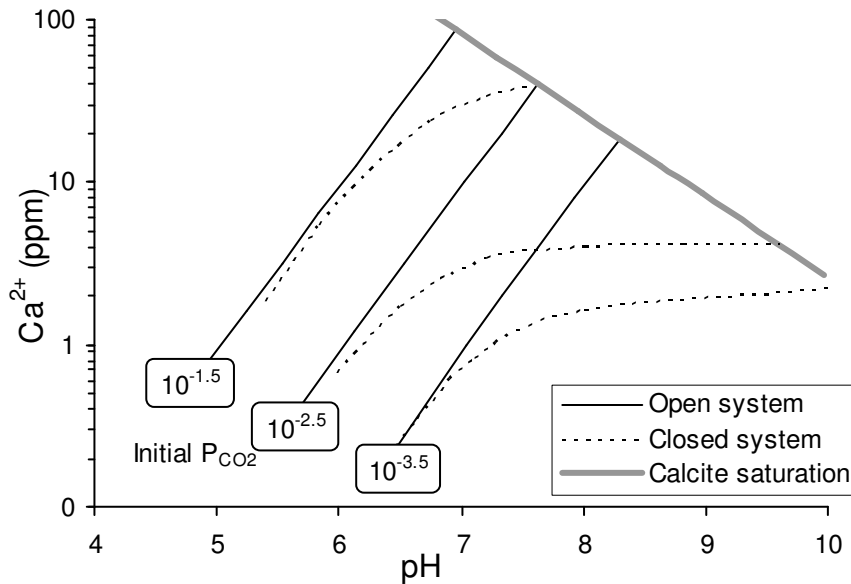


Fig. 5-1 The evolution of pH and Ca^{2+} (a measure of calcite dissolution) as groundwater dissolves calcite under open and closed system conditions, for varying initial P_{CO_2} conditions. The continual access to soil CO_2 under open system conditions allows considerably more calcite to be dissolved than for closed system conditions.

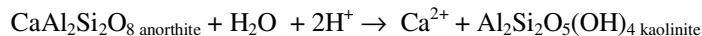
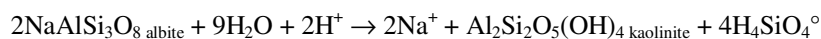
WEATHERING IN SILICATE TERRAINS

Differential crystallization during cooling of siliceous magma generates a series of high temperature silicate and aluminum silicate minerals, which form most of the Earth's crust (Chapter 1, Silicates). The higher temperature mineralogy is dominated by ferromagnesian silicates including olivine $[(\text{Fe},\text{Mg})_2\text{SiO}_4]$ and pyroxene $[\text{Ca}(\text{Mg},\text{Fe})\text{Si}_2\text{O}_6]$, and the calcium rich feldspar, anorthite $[\text{CaAl}_2\text{Si}_2\text{O}_8]$. The alkalis, Na and K, crystallize as later stage (lower temperature) ferromagnesian minerals — amphibole $[\text{Ca}_2(\text{Na})(\text{Mg},\text{Fe},\text{Al})_5[(\text{Al},\text{Si})_4\text{O}_{11}]_2(\text{OH})_2]$ and biotite $[(\text{Mg},\text{Fe})_3(\text{AlSiO}_{10})(\text{OH})_2]$, and as alkali feldspars — albite $[\text{NaAlSi}_3\text{O}_8]$ and orthoclase $[\text{KAlSi}_3\text{O}_8]$. The residual melt, rich in aluminum, silica and potassium, forms muscovite $[\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2]$ and quartz $[\text{SiO}_2]$.

Weathering of these high temperature minerals releases cations and silica while forming an array of more stable aluminum silicate clay minerals. Al-free ferromagnesian silicates weather through congruent dissolution reactions, releasing Mg^{2+} , Fe^{2+} and silicic acid to solution. By contrast, the aluminum silicates dissolve incongruently, forming Al-Si clays and releasing Ca^{2+} , Na^+ and K^+ as well as some silicic acid to solution. All silicate alteration reactions are acid consuming. Alteration is greatest under open system conditions in soils where high carbonic acid from the degradation of organics is available. Acidity is also contributed by organic acids generated during the breakdown of biomass in soils, as discussed in Chapter 3. Equilibrium, however, is rarely attained. Only at very high pH and high cation activities do thermodynamics favor precipitation of feldspars or other primary silicate minerals at low temperature.

Weathering of aluminum silicate minerals

Feldspar is the most common mineral in the Earth's crust, and is by far the dominant phase in silicate weathering reactions. Weathering releases cations to solution, according to incongruent dissolution reactions, e.g.:

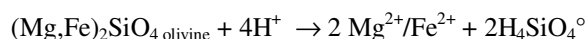
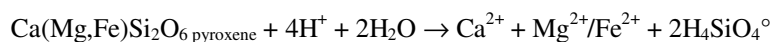


Acidity is an essential component, as the formation of clays like kaolinite requires H^+ to form hydroxide from structural oxygen. These reactions are typically referred to as silicate hydrolysis reactions. Silica is released to solution by the weathering of the alkali feldspars (Na and K) but not by the weathering of anorthite in which an extra Al^{3+} replaces one Si^{4+} to maintain the charge balance with divalent Ca^{2+} .

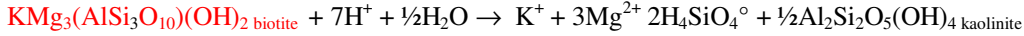
The alteration of these high-temperature feldspars and formation of low-temperature clay minerals (incongruent dissolution) is such that equilibrium with primary mineral phases is seldom reached. Only under conditions of high pH and high solute concentration is thermodynamic equilibrium attained. In the near surface environment where water circulation is relatively rapid, weathering will continue providing there is a source of acidity to drive the reactions. For the alkali feldspars, the concentrations of Na^+ and K^+ can be used as an indication of the extent of weathering, as there are few mineralogical controls on their concentrations. For anorthite, Ca^{2+} concentrations are generally limited by calcite saturation.

Weathering of ferromagnesian silicates

Weathering of the ferromagnesian silicates such as pyroxene and olivine proceeds congruently, with release of silica, ferrous iron, Fe^{2+} and/or Mg^{2+} to solution:



As these minerals contain no aluminum, clay minerals like kaolinite do not form. Only under conditions of low water/rock ratios will secondary phases such as serpentine



Dissolution of quartz [SiO_2], the second most abundant silicate mineral in the crust, is kinetically impeded and contributes little to solution at low temperature. As $a_{\text{H}_4\text{SiO}_4^\circ}$ increases through the weathering of silicate minerals, quartz solubility is readily exceeded. Silicic acid will also exceed the solubility of chalcedony and opal — polymorphs of quartz with the same chemical formula but a different structure and higher solubility. The solubility of silicic acid is ultimately limited by amorphous silica gel [H_4SiO_4] which can precipitate at low temperature. Over time, this phase can recrystallize into more stable opal [$\text{SiO}_2 \cdot n(\text{H}_2\text{O})$], a hydrated form ($n < 1$) with little to no crystallinity. Opal can also be directly precipitated from solution, for example, in plant cells as phytoliths. With increased temperature and time, amorphous to poorly crystalline silica forms transform to chalcedony [SiO_2] — a microcrystalline form of quartz. The solubility of quartz and its polymorphs, however, are very much temperature dependent (Fig. 5-2). The solubility curves for chalcedony and quartz are useful at geothermal temperatures (greater than 100°C) where the kinetics of their dissolution and precipitation are greatly increased. A further control on amorphous silica solubility is pH. In Chapter 2, Fig. 2-6 shows the increased state of ionization for silicic acid at high pH, which greatly increases its solubility. Fig. 5-2 (right) shows this effect, where the solubility of amorphous silica increases from less than 200 ppm in neutral pH waters to very high levels near pH 10.

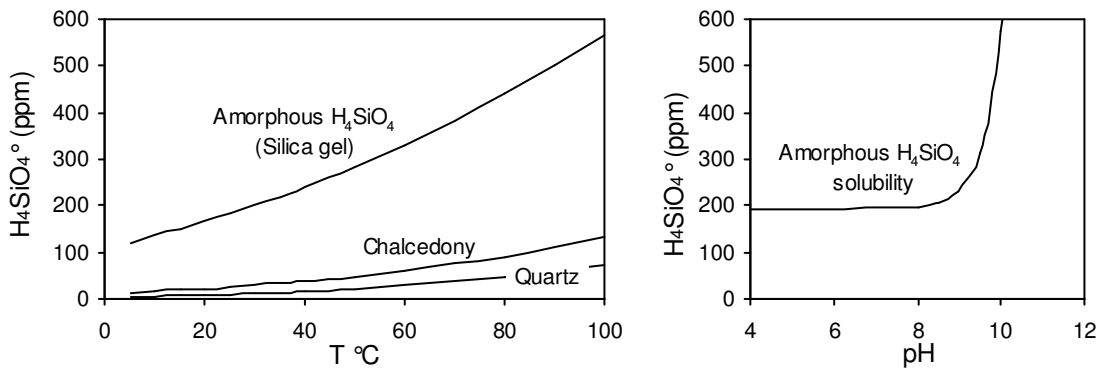


Fig. 5-2 Solubility of quartz [SiO_2] and its polymorphs with temperature (left) and pH (right).

Although silica has an apparently high solubility in natural waters, values seldom exceed about 50 ppm, and are more commonly in the range of 10 to 30 ppm. This is due to the low rate of silicate mineral weathering, particularly under closed system conditions which limits the amount of acidity available. It is also due to the sorption of silicic acid on mineral surfaces and organics in soils.

The acidity available for weathering is largely determined by the P_{CO_2} conditions that exist in the recharge area. Organic acids and oxidation of sulfide minerals also contribute H^+ ions. The slow rates of silicate weathering are such that much may take place under closed system conditions below the water table. If no subsurface sources of CO_2 (e.g. oxidation of methane, or metamorphic CO_2) or other acids (e.g. H_2SO_4 from oxidation of pyrite) are available, then P_{CO_2} will drop to very low levels and pH will increase to values as high as 10 or higher. An example of such a case comes from the Ahouse geothermal spring on the Pacific coast of southern Canada, which was introduced in Chapter 3 as a case study for alkalinity.

Example 5-3 Closed system weathering in silicic terrain

Recall that the Ahouse geothermal waters discharge from a quartz diorite (quartz [SiO₂] and albite [NaAlSi₃O₈]) pluton on the west coast of Vancouver Island. The temperature is 23°C, about 10°C above the average annual temperature, indicating a depth of circulation of at least 500 m. Concentrations are in mmol/L:

Ahouse geothermal water, T = 23°C		pH = 10.05								
	HCO ₃ ⁻	CO ₃ ²⁻	SO ₄ ²⁻	Cl ⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Si _{total}	
ppm	15.8	8.24	11.7	10.1	1.91	0.12	32.6	0.18	9.01	
mmol/kg	0.259	0.137	0.12	0.29	0.048	0.005	1.42	0.0051	0.30	

The high pH, Na⁺ and SiO₂ indicate extensive weathering of the host silicate rocks. The absence of significant Ca²⁺ precludes dissolution of calcite that can occur in fractures within silicate rocks. Note that the high sodium is not “supported” by Cl⁻, which may come from sea spray this coastal setting (Na/Ca molar ratio in seawater is 0.92). Most of the Na⁺ is then rock-derived. A correction for Na⁺ from sea spray ($m_{\text{Na}^+}/m_{\text{Cl}^-} = 0.86$) can be made by subtracting this amount from the measured Na⁺ ($1.42 - 0.86 \times 0.29 = 1.17$ mmol/kg).

The reaction constant for alteration of NaAlSi₃O₈ albite to Al₂Si₂O₅(OH)₄ kaolinite from above is determined from values for ΔG° (Table 2-5):

$$\begin{aligned}\Delta G_r^\circ &= 2\Delta G_{\text{Na}^+}^\circ + \Delta G_{\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4}^\circ + 4\Delta G_{\text{H}_4\text{SiO}_4}^\circ - 2\Delta G_{\text{NaAlSi}_3\text{O}_8}^\circ - 9\Delta G_{\text{H}_2\text{O}}^\circ \\ &= 2 \cdot (-262.0) + (-3799.7) + 4 \cdot (-1307.9) - 2 \cdot (3711.5) - 9 \cdot (-237.14) \\ &= -1.96\end{aligned}$$

$$\log K = -\frac{\Delta G_r^\circ}{5.708} = \frac{-1.96}{5.708} = -0.34$$

$$K = 10^{-0.34} = \frac{a_{\text{Na}^+}^2 \cdot a_{\text{H}_4\text{SiO}_4}^4}{a_{\text{H}^+}^2}$$

This relationship defines the activities of Na⁺, silicic acid and pH for equilibrium between albite and kaolinite. It shows the inverse relationship between acidity and the dissolved products of weathering. Rewriting it in logarithmic format, and using the Na⁺/H⁺ ratio as an index of the extent of weathering allows the reaction of albite to kaolinite to be visualized graphically.

$$\log \frac{a_{\text{Na}^+}}{a_{\text{H}^+}} = -2 a_{\text{H}_4\text{SiO}_4} - 0.17$$

This equation defines the boundary between albite and kaolinite. In the recharge area at low pH (high a_{H^+}) and low Na⁺ concentration, kaolinite is the stable phase. Above this line, at high pH and high Na⁺ activity, albite is stable and this weathering reaction will stop. The small open circles in Fig. 5-3 show the geochemical evolution during albite weathering from the initial condition, with an increase in the activities of both Na⁺ and silicic acid and increase in pH.

The Ahouse waters can be plotted on this diagram to evaluate the extent of albite weathering. The activity of Na⁺ is determined using its concentration (32.6 ppm), corrected for Cl⁻-supported Na⁺ from seawater ($\text{Na}^+_{\text{rock}} = 26.7$ ppm) and the ionic strength ($I = 0.0017$), giving $a_{\text{Na}^+_{\text{rock}}} = 0.0011$. With pH 10.05, this gives a value for $\log(a_{\text{Na}^+_{\text{rock}}}/a_{\text{H}^+}) = 7.09$, and silicic acid activity, $a_{\text{H}_4\text{SiO}_4} = 0.00028$. This water plots just above the line for albite-kaolinite equilibrium indicating that weathering in this system has proceeded to the full extent for the given initial conditions.

How much acid was required for this weathering?

The degree of weathering is defined by the available acid. In the case of albite weathering, one mole of H^+ is required for each mole of $NaAlSi_3O_5$ dissolved and Na^+ released. From the amount of Na^+ released from the rock:

$$\begin{aligned} Na^+_{\text{rock}} &= 26.7 \text{ ppm} \\ m_{Na^+_{\text{rock}}} &= 0.0012 \text{ moles/kg} \\ H^+ \text{ consumed by weathering} &= 0.0012 \text{ moles/kg} \\ \text{initial pH} &= 2.93 \end{aligned}$$

This amount of acidity, if gained in one shot, would give an initial pH of the recharge waters of 2.9, which would make a rather acidic soil. More likely, this amount of acidity has been gained through open system weathering in the recharge area, where the acidity was continually supplied from the unsaturated zone.

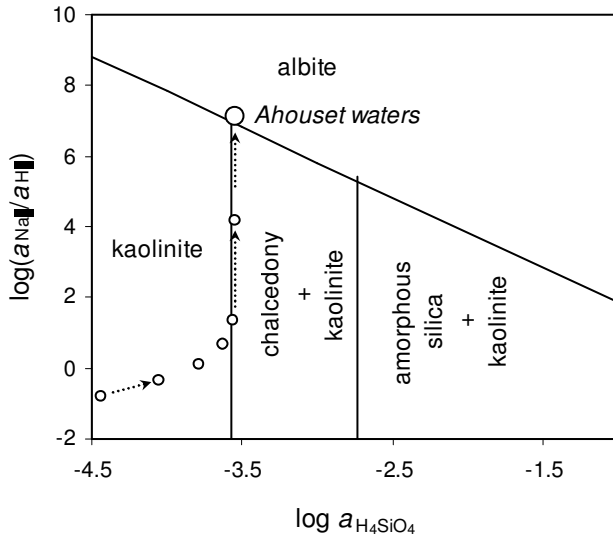


Fig. 5-3 Mineral stability diagram for Na^+ and silicic acid with pH

How much silica was produced by weathering?

The amount of silicic acid produced from albite weathering, like Na^+ can be calculated from the stoichiometry of the albite alteration reaction. Two moles of $H_4SiO_4^0$ are released per mole of albite dissolved, and so according to the extent of albite weathering from the calculations above,

$$\begin{aligned} m_{Na^+_{\text{rock}}} &= 0.0012 \text{ moles/kg} \\ m_{H_4SiO_4^0_{\text{total}}} &= 0.0023 \text{ moles/kg} \\ &= 74.2 \text{ ppm Si} \\ \log a_{H_4SiO_4^0_{\text{total}}} &= -2.63 \end{aligned}$$

This amount of dissolved silica is much greater than that which is measured for these waters (9.01 ppm Si or 0.30 mol/kg). This missing silica has precipitated from solution in the subsurface. Fig. 5-3 shows that these waters plot essentially on the boundary for chalcedony ($K_{\text{chalc.}} = -3.58$ at 25°C), a silica mineral that commonly precipitates from thermal waters. As the thermal waters dissolved albite, the dissolved silica concentration increased until this boundary was reached. At this point, additional silica was precipitated as chalcedony, the mineralogical control on $a_{H_4SiO_4^0}$ in this system, and the evolution of the Ahouset waters followed this line vertically as weathering proceeded to their final composition.

What was the source of acidity?

The potential contributors of the 0.00116 mol/kg of H^+ required for weathering in this system include carbonic acid from the soil, organic acids in the soil (which ultimately produce CO_2) and oxidation of

pyrite (11.7 ppm SO_4^{2-}). Let's look first at carbonic acid. The carbonate alkalinity and concentration of dissolved inorganic carbon species in these waters, determined in Chapter 3 from alkalinity corrected for H_3SiO_4^- and OH^- , are:

$$\begin{aligned} \text{alk}_C &= 0.00053 \text{ eq/kg} \\ m_{\text{HCO}_3^-} &= 0.00026 \text{ mol/kg} \\ m_{\text{CO}_3^{2-}} &= 0.00014 \text{ mol/kg} \\ \text{DIC} &= 0.00040 \text{ mol/kg} \end{aligned}$$

The final carbonic acid concentration and P_{CO_2} are determined from pH and bicarbonate:

$$\begin{aligned} K_1 &= \frac{a_{\text{HCO}_3^-} \cdot a_{\text{H}^+}}{a_{\text{H}_2\text{CO}_3}} = 10^{-6.35} \\ a_{\text{H}_2\text{CO}_3} &= \frac{0.00026 \cdot 10^{-10.05}}{10^{-6.35}} = 5.2 \cdot 10^{-8} \\ K_{\text{CO}_2} &= \frac{a_{\text{H}_2\text{CO}_3}}{P_{\text{CO}_2}} = 10^{-1.47} \\ P_{\text{CO}_2} &= \frac{5.2 \cdot 10^{-8}}{10^{-1.47}} = 1.54 \cdot 10^{-5} = 10^{-5.82} \end{aligned}$$

Attributing the final DIC to CO_2 dissolved during recharge, we can calculate the total carbonic acid. If this was incorporated before weathering began, then a P_{CO_2} can also be estimated:

$$\begin{aligned} m_{\text{H}_2\text{CO}_3 \text{ initial}} &= \text{DIC}_{\text{current}} = 0.00040 \text{ mol/kg} \\ P_{\text{CO}_2 \text{ initial}} &= \frac{0.00040}{10^{-1.47}} = 10^{-1.93} \end{aligned}$$

While this P_{CO_2} is close to what one would expect for soils in the humid west coast of Vancouver Island where these springs are found, the carbonic acid concentration is not sufficient to account for the observed weathering. The total concentration of acidity released from carbonic acid is equal to the total carbonate alkalinity, $\text{alk}_C = m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} = 0.00053 \text{ eq/kg}$, which is less than half of the acidity determined to have been consumed.

Acidity has also been provided to this water from the dissociation of silicic acid ($m_{\text{H}_3\text{SiO}_4^-} = 0.00019 \text{ mol/kg}$) and from the dissociation of water ($m_{\text{OH}^-} = 0.00011 \text{ mol/kg}$), which brings the accounting of available acid to 0.00083 mol/kg. This, however, is still less than the 0.0012 mol/kg H^+ which was consumed by weathering.

The balance of the acidity could be attributed to sulfuric acid, which is accounted for by the sulfate found in this water ($m_{\text{SO}_4^{2-}} = 0.00012 \text{ mol/kg}$ or 0.00024 eq/kg). As two moles of H^+ are produced by dissociation of each mole of H_2SO_4 , a total of 0.000244 moles of acidity can be attributed to sulfate in the Ahouset waters. While sulfate can originate in sulfate minerals such as gypsum [$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$], this is unlikely at Ahouset due to the low concentration of Ca^{2+} in the water. Moreover, sulfur isotopes provide further evidence of a sulfide origin. A value for $\delta^{34}\text{S}_{\text{SO}_4^{2-}}$ of +2.6‰, is within the range anticipated for sulfide minerals.

The total acidity that has been consumed during weathering by this water can then be accounted for as:

$$\begin{aligned} m_{\text{H}^+ \text{ weathering}} &= m_{\text{Na}^+ \text{ rock}} = m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + 2m_{\text{SO}_4^{2-}} + m_{\text{H}_3\text{SiO}_4^-} + m_{\text{OH}^-} \\ &= 0.00026 + 0.00027 + 0.00025 + 0.00019 + 0.00011 \end{aligned}$$

This amounts to 0.0011 mol/kg H^+ , which is acceptably close to the acidity of 0.0012 mol/kg H^+ determined from the concentration of Na^+ released by albite weathering.

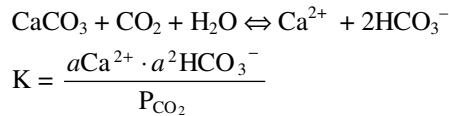
CONTROLS ON CALCITE SOLUBILITY

Calcite [CaCO_3] is a carbonate mineral that readily forms and dissolves at low temperatures, and so represents an important control on the concentration and speciation of DIC. Other important carbonate minerals include dolomite [$\text{CaMg}(\text{CO}_3)_2$] and high magnesium calcite [$\text{Ca}_{(>0.8)}\text{Mg}_{(<0.2)}(\text{CO}_3)_2$]. Although dolomite is often supersaturated in many waters, its formation is generally restricted to hypersaline and/or higher temperature settings such as sabkhas and marine sediments where calcite precipitation has already lowered Ca^{2+} concentrations.

The dissolution or precipitation of calcite is obviously sensitive to the activity of dissolved carbonate $a\text{CO}_3^{2-}$, which is controlled in part by pH. The role of P_{CO_2} is also important as this affects the concentration DIC. In the following, we will look at the effect of both pH and P_{CO_2} on calcite solubility. The examples used will show how the evolution of these two parameters can control calcite solubility, and hence DIC concentrations and speciation.

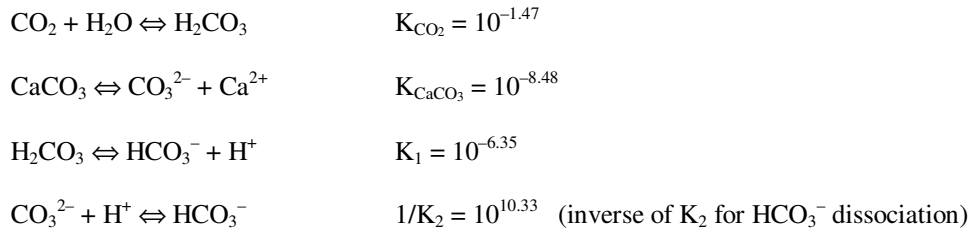
P_{CO_2} and calcite solubility

The weathering of limestone by carbonic acid was presented above according to the reaction:



which shows that the solubility of calcite will be affected by P_{CO_2} .

This calcite dissolution reaction is simply the addition of the reactions:



and for which the overall reaction constant is equal to the product of all four individual reaction constants:

$$K = 10^{-1.47} \cdot 10^{-8.48} \cdot 10^{-6.35} \cdot 10^{10.33} = 10^{-5.97}$$

and so $10^{-5.97} = \frac{a\text{Ca}^{2+} \cdot a^2\text{HCO}_3^-}{P_{\text{CO}_2}}$

This reaction constant allows us to look at the solubility of calcite as a function of P_{CO_2} . To do so, either $a\text{HCO}_3^-$ or $m\text{Ca}^{2+}$ must be set at a constant value. This is done in Fig. 5-4 where P_{CO_2} is plotted against HCO_3^- for $m\text{Ca}^{2+} = 2$ mmol/kg, giving the conditions for which calcite is at the point of saturation. Unilateral increases or decreases in P_{CO_2} will then cause calcite to dissolve or precipitate from solution. A practical example of the latter is when bicarbonate groundwaters are brought to the surface either by sampling or at a discharge site. In contact with the atmosphere ($P_{\text{CO}_2} = 10^{-3.4}$), the water will degas CO_2 in

order to establish an equilibrium with the new conditions. Precipitation of calcite, either in the sample bottle or at the spring vent is the consequence.

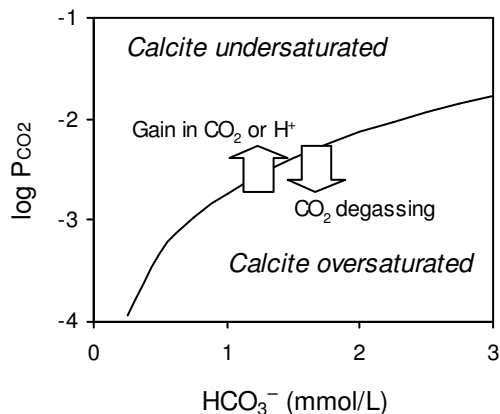
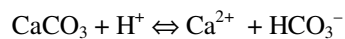


Fig. 5-4 Calcite saturation as a function of P_{CO_2} and bicarbonate alkalinity. This diagram is calculated with $m_{\text{Ca}^{2+}} = 2 \text{ mm/kg}$. CO_2 degassing across a free surface, such as at spring vents or over surface waters with $P_{\text{CO}_2} > 10^{-3.4}$, will provoke calcite supersaturation and precipitation. Gains of CO_2 from aerobic oxidation of organic carbon or from geogenic sources of CO_2 (volcanic, metamorphic) cause calcite undersaturation.

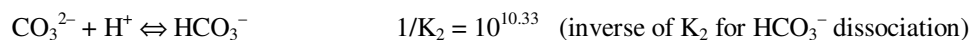
pH and calcite solubility

The calcite dissolution reaction above can also be written in terms of acidity, rather than P_{CO_2} :



$$K = \frac{a_{\text{Ca}^{2+}} \cdot a_{\text{HCO}_3^-}}{a_{\text{H}^+}}$$

Written in this fashion shows the control of pH on calcite solubility. This reaction is the sum of only two fundamental carbonate reactions:



and the overall reaction constant is:

$$K = 10^{-8.48} \cdot 10^{10.33} = 10^{1.85} = \frac{a_{\text{Ca}^{2+}} \cdot a_{\text{HCO}_3^-}}{a_{\text{H}^+}}$$

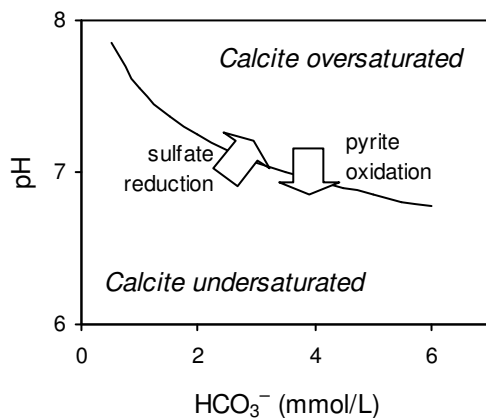


Fig. 5-5 Calcite saturation as a function of pH and bicarbonate alkalinity, calculated with $m\text{Ca}^{2+}$ fixed at 2 mmol/kg. Sulfide oxidation and sulfate reduction (by oxidation of organics to HCO_3^-) are given as examples of aqueous reactions with a direct effect on pH.

Plotted in Fig. 5-5, this reaction shows the sensitivity of calcite saturation to pH. Hence, calcite dissolution and precipitation is easily provoked by shifts in pH as well as by gains or losses of bicarbonate. Increases in pH accompany mineral weathering reactions and so alteration of Ca-feldspars (anorthite) and other Ca-silicate minerals will eventually cause calcite saturation and supersaturation. Other important acid-producing and consuming reactions are redox reactions (discussed in the following chapter). Oxidation of sulfides such as pyrite, and oxidation of Fe^{2+} by O_2 are common acid-generating reactions. On the other hand, reduction of sulfate to sulfide and other reducing reactions will consume H^+ and cause calcite to precipitate.

CARBON-13 AND DIC EVOLUTION

Tracing the carbon cycle and evolution of DIC in waters is greatly aided by measurements of carbon isotopes. Most of the DIC in groundwaters originates as CO_2 from the degradation of soil organics by bacteria. The origin of DIC in surface waters can include soil-derived CO_2 which is transported to rivers and lakes by runoff and shallow groundwater. However, open water bodies will exchange their DIC with the atmosphere and eventually equilibrate with this low P_{CO_2} source. Surface waters will also host in-situ biogeochemical reactions including photosynthesis and bacterial respiration of organics, depending on nutrient conditions. In all these settings, the $\delta^{13}\text{C}$ of DIC can be modified, and tells a part of the story of the geochemical evolution of DIC.

Atmospheric CO_2 dissolved by precipitation and runoff is soon masked by the much greater reservoir of CO_2 found in soils. The high P_{CO_2} of soils generated by the bacterial degradation of dead biomass also differs from atmospheric CO_2 in its $\delta^{13}\text{C}$, which is much more negative. As discussed in Chapter 3, photosynthesis is highly discriminating, giving C_3 plant material a $\delta^{13}\text{C}$ value of about -27% . Soil CO_2 , however, has a slightly modified value, due to the outward diffusion from high P_{CO_2} in soils. As ^{12}C is more diffusive, this imparts a slight enrichment on the remaining soil CO_2 (Cerling et al., 1991). In most C_3 landscapes, the soil CO_2 has $\delta^{13}\text{C} \sim -23\%$.

^{13}C of DIC during groundwater recharge

During infiltration, recharge water dissolves soil $\text{CO}_{2(\text{g})}$ to produce $\text{CO}_{2(\text{aq})}$, which hydrates to H_2CO_3 and dissociates into HCO_3^- . Recall from above that while H_2CO_3 is used in thermodynamic calculations, this species occurs mainly in its unhydrated form $\text{CO}_{2(\text{aq})}$. During CO_2 dissolution and hydration, ^{13}C is preferentially partitioned into the hydrated species. Thus, HCO_3^- has more ^{13}C than $\text{CO}_{2(\text{aq})}$. The ^{13}C content

of the dissolved CO_2 ($\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$) is about 1‰ lower than that of the soil CO_2 ($\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$) while $\delta^{13}\text{C}_{\text{HCO}_3^-}$ is about 10‰ greater than $\text{CO}_2(\text{g})$. If the pH of the soil water is below about 6.4, the DIC is comprised mainly of $\text{CO}_2(\text{aq})$ and so $\delta^{13}\text{C}_{\text{DIC}}$ will be close to the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$. At greater pH values it is mainly HCO_3^- and so $\delta^{13}\text{C}_{\text{DIC}}$ will be closer to $\delta^{13}\text{C}_{\text{CO}_2(\text{g})} + 10\%$. This is illustrated in Fig. 5-6.

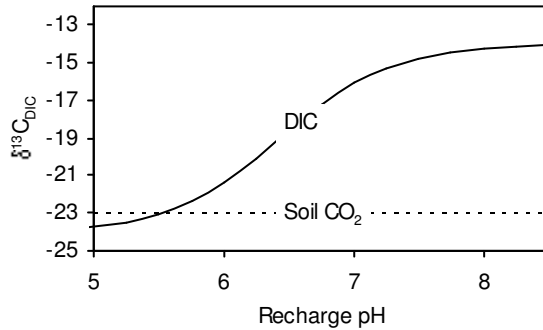


Fig. 5-6 Effect of recharge pH on the $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC) in equilibrium with soil CO_2 (open system conditions). Calculated for case where $\delta^{13}\text{C}$ of soil CO_2 is -23% at 15°C .

The precise value for $\delta^{13}\text{C}_{\text{DIC}}$ will depend on pH, which controls the ratio of $\text{CO}_2(\text{aq})$ to HCO_3^- . Temperature also plays a role as it affects the $\text{CO}_2(\text{g}) - \text{HCO}_3^-$ enrichment factor ($\epsilon^{13}\text{C}_{\text{HCO}_3-\text{CO}_2(\text{g})}$). Values for the $\delta^{13}\text{C}$ of DIC during recharge at different temperatures and pH are given in Table 5-1, calculated according to the isotope mass balance equation:

$$\delta^{13}\text{C}_{\text{DIC}} = \left(\frac{m_{\text{HCO}_3^-}}{m_{\text{DIC}}} \right) \cdot (\delta^{13}\text{C}_{\text{CO}_2} + \epsilon^{13}\text{C}_{\text{H}_2\text{CO}_3-\text{CO}_2}) + \left(\frac{m_{\text{CO}_2}}{m_{\text{DIC}}} \right) \cdot (\delta^{13}\text{C}_{\text{CO}_2} + \epsilon^{13}\text{C}_{\text{HCO}_3-\text{CO}_2})$$

Table 5-1 $\delta^{13}\text{C}_{\text{DIC}}$ of recharge water for different temperatures and pH

T	pH	$\frac{\text{HCO}_3^-}{\text{H}_2\text{CO}_3}$	$\delta^{13}\text{C}_{\text{soil CO}_2}$	$\epsilon_{\text{H}_2\text{CO}_3-\text{CO}_2}$	$\epsilon_{\text{HCO}_3-\text{CO}_2}$	$\delta^{13}\text{C}_{\text{DIC}}$
5	5.5	0.10	-23	-1.2	10.2	-23.1
5	6.5	0.97	-23	-1.2	10.2	-18.5
5	7.5	9.7	-23	-1.2	10.2	-13.8
15	5.5	0.12	-23	-1.1	9.0	-23.0
15	6.5	1.2	-23	-1.1	9.0	-18.6
15	7.5	12	-23	-1.1	9.0	-14.7
25	5.5	0.14	-23	-1.1	7.9	-23.0
25	6.5	1.4	-23	-1.1	7.9	-18.9
25	7.5	14	-23	-1.1	7.9	-15.7

note: $\epsilon^{13}\text{C}_{\text{H}_2\text{CO}_3-\text{CO}_2} = -0.373 (10^3 \text{T}^{-1}) + 0.19$ (Table 3-3; Vogel et al., 1970)
 $\epsilon^{13}\text{C}_{\text{HCO}_3-\text{CO}_2} = 9.552 (10^3 \text{T}^{-1}) - 24.10$ (Table 3-3; Mook et al., 1974)

Accordingly, DIC and $\delta^{13}\text{C}_{\text{DIC}}$ in groundwater evolve to higher values during weathering reactions in the soil or aquifer. Controls on this evolution include whether open or closed system conditions prevail, and whether the parent material is silicate or carbonate. Each weathering scenario will support a different evolution for DIC and $\delta^{13}\text{C}_{\text{DIC}}$.

Evolution of $\delta^{13}\text{C}_{\text{DIC}}$ in carbonate aquifers

If weathering reactions take place under open system conditions during recharge in carbonate terrains, the $\delta^{13}\text{C}$ of the DIC is simply controlled by the soil CO_2 and the pH (which is determined by the P_{CO_2} , see Example 5-1). Even as the soil waters are dissolving calcite with a $\delta^{13}\text{C}$ value of say 0‰, exchange between the DIC and the much greater reservoir of soil CO_2 recycle the aquifer carbonate and maintains a $\delta^{13}\text{C}_{\text{DIC}}$ in equilibrium with the soil CO_2 . Accordingly, the final $\delta^{13}\text{C}_{\text{DIC}}$ after weathering reactions can be determined from Table 5-1.

On the other hand, if carbonate weathering takes place under closed system conditions, exchange with soil CO_2 will not occur and so the initial $\delta^{13}\text{C}_{\text{DIC}}$ value will increase as ^{13}C -enriched DIC is gained from bedrock. This will happen not only in limestone aquifers but in silicate aquifers as well where calcite may be present as a fracture mineral (metamorphic or hydrothermal calcite), or as carbonate grains, cobbles or cement in clastic aquifers. Most marine carbonates have $\delta^{13}\text{C} \approx 0 \pm 1\%$ VPDB, although some can extend to $\pm 5\%$. Carbonate minerals in igneous and metamorphic rocks have $\delta^{13}\text{C}$ values of 0 to -10% .

The difference between these two scenarios can be seen in the following example, where the final $\delta^{13}\text{C}$ of the DIC after dissolution of limestone to the point of calcite saturation.

Example 5-4 $\delta^{13}\text{C}_{\text{DIC}}$ following limestone dissolution

What is the final $\delta^{13}\text{C}$ value of DIC after dissolving marine limestone under open system conditions, assuming an initial P_{CO_2} of $10^{-1.5}$, $\delta^{13}\text{C}_{\text{soil CO}_2} = -23\%$ and temperature = 25°C .

If recharge occurs under open system conditions, then the final $\delta^{13}\text{C}_{\text{DIC}}$ is determined by the final pH and the fractionation of ^{13}C between the soil CO_2 and DIC species (H_2CO_3 and HCO_3^-) at that pH. From Example 5-1 the pH was 6.93 for calcite dissolution under open system conditions with $P_{\text{CO}_2} = 10^{-1.5}$.

First, we should determine the relative proportions of H_2CO_3 and HCO_3^- :

$$\text{from: } K_1 = \frac{m_{\text{HCO}_3^-} \cdot m_{\text{H}^+}}{m_{\text{H}_2\text{CO}_3}} = 10^{-6.35}$$

$$\text{we know that: } \frac{m_{\text{HCO}_3^-}}{m_{\text{H}_2\text{CO}_3}} = \frac{10^{-6.35}}{10^{-6.93}} = 3.8$$

$$\text{from Example 5-1: } m_{\text{HCO}_3^-} = 2.04 \times 2 = 4.1 \text{ mmol/L}$$

$$\text{so: } m_{\text{H}_2\text{CO}_3} = \frac{4.1}{3.8} = 1.8 \text{ mmol/L}$$

Then using an isotope mass balance equation and $\epsilon^{13}\text{C}$ values from Table 5-1:

$$\begin{aligned} m_{\text{DIC}} (\delta^{13}\text{C}_{\text{DIC}}) &= m_{\text{H}_2\text{CO}_3} (\delta^{13}\text{C}_{\text{CO}_2} + \epsilon_{\text{H}_2\text{CO}_3\text{-CO}_2}) + m_{\text{HCO}_3^-} (\delta^{13}\text{C}_{\text{CO}_2} + \epsilon_{\text{HCO}_3\text{-CO}_2}) \\ &= 1.8 (-23 - 1.1) + 4.1 (-23 + 7.9) \\ &= -105.3 \end{aligned}$$

$$\delta^{13}\text{C}_{\text{DIC}} = \frac{-105.3}{m_{\text{DIC}}} = \frac{-105.3}{1.8 + 4.1} = -17.8\%$$

This value can also be found on the graph in Fig. 5-6 for the given pH of 6.93.

Now what would this value be if calcite dissolution takes place under closed system conditions?

In the closed system case, the final $\delta^{13}\text{C}_{\text{DIC}}$ is a mixture of the initial $\delta^{13}\text{C}_{\text{DIC}}$ established in the soil before dissolving any calcite, and the amount of calcite dissolved in the aquifer. These two contributions can be determined according to the calculations used in Example 5-2 where the initial DIC was $m_{\text{H}_2\text{CO}_3} + m_{\text{HCO}_3^-} = 1.07 + 0.022 = 1.09$ mmol/L, the pH was 4.66, and the amount of calcite dissolved was 1.1 mmol/L.

Using the isotope mass balance equation from above:

$$m_{\text{DIC}} (\delta^{13}\text{C}_{\text{DIC}}) = m_{\text{H}_2\text{CO}_3} (\delta^{13}\text{C}_{\text{CO}_2} + \epsilon_{\text{H}_2\text{CO}_3\text{-CO}_2}) + m_{\text{HCO}_3^-} (\delta^{13}\text{C}_{\text{CO}_2} + \epsilon_{\text{HCO}_3\text{-CO}_2}) + m_{\text{CaCO}_3} (\delta^{13}\text{C}_{\text{CaCO}_3})$$

$$\delta^{13}\text{C}_{\text{DIC}} = \frac{1.07(-23 - 1.1) + 0.022(-23 + 7.9) + 1.1(0)}{1.09 + 1.1}$$

$$= -11.9\text{‰}$$

In both cases, the DIC after carbonate weathering is more enriched in ^{13}C than the initial DIC. However, the enrichment under closed system conditions is due to mixing with the initial DIC from the soil and the DIC from calcite dissolution, and is much more significant (-11.9‰ compared to -17.8‰) than seen for open system evolution.

In real systems, DIC evolution usually takes place under partially open conditions, where some calcite or other carbonate mineral is dissolved in the unsaturated zone, and continues below the water table under closed system conditions. In this case, the final measured $\delta^{13}\text{C}_{\text{DIC}}$ will be intermediary between the two end-members calculated in the example.

Evolution of $\delta^{13}\text{C}_{\text{DIC}}$ in silicate aquifers

The change in $\delta^{13}\text{C}$ during weathering of silicate minerals is less complicated than in carbonate aquifers, as the only source of carbon is the soil CO_2 . As a consequence, the only controlling factor is the pH at the point that the recharge waters enter closed system conditions. After this point, the $\delta^{13}\text{C}_{\text{DIC}}$ will not change, even as the pH continues to increase, providing no subsurface sources of carbonate are encountered.

The pH under open system weathering of silicate minerals such as feldspars is controlled by the P_{CO_2} in the unsaturated zone.

$\delta^{13}\text{C}$ of DIC in surface waters

Rivers and lakes fed by shallow groundwaters and runoff through soils will have a DIC with $\delta^{13}\text{C}$ that has evolved under mostly open system conditions, i.e. -20 to -15‰ (Fig. 5-6). If carbonate weathering is occurring in the catchment, then $\delta^{13}\text{C}_{\text{DIC}}$ will be proportionately enriched, with values approaching -10‰ .

Exchange with atmospheric CO_2 ($\text{P}_{\text{CO}_2} = 10^{-3.4}$; $\delta^{13}\text{C} = -7.5\text{‰}$) will attenuate the P_{CO_2} in the water column and increase the $\delta^{13}\text{C}_{\text{DIC}}$. In lakes with residence times that exceed a few years, the $\delta^{13}\text{C}_{\text{DIC}}$ will approach an equilibrium value, which depends on pH and temperature.

Example 5-5 $\delta^{13}\text{C}$ of surface water DIC in equilibrium with atmospheric CO_2

The $\delta^{13}\text{C}_{\text{DIC}}$ of surface water from Lake Ontario ($T = 15^\circ\text{C}$, $\text{pH} = 7$, $\text{HCO}_3^- = 8 \times 10^{-4}$) was found to be -1‰ . Is this due to exchange with atmospheric CO_2 or are other processes involved.

From Table 5-1, the enrichment factors for ^{13}C during $\text{CO}_2(\text{g}) - \text{DIC}$ exchange are :

$$\begin{aligned}\epsilon^{13}\text{C}_{\text{HCO}_3^- - \text{CO}_2(\text{g})} &= 9.0\text{‰} \\ \epsilon^{13}\text{C}_{\text{H}_2\text{CO}_3 - \text{CO}_2(\text{g})} &= -1.1\text{‰}\end{aligned}$$

Following the equations from Chapter 4, and using an alkalinity of 1 for convenience (page XX), the DIC speciation at pH 7 is:

$$\begin{aligned}m\text{HCO}_3^- &= \frac{K_1}{K_1 + 10^{-\text{pH}}} = \frac{10^{-6.42}}{10^{-6.42} + 10^{-7}} = 0.79 \text{ or } 79\% \\ m\text{H}_2\text{CO}_3 &= 1 - m\text{HCO}_3^- = 0.21\end{aligned}$$

and substituting the molar fractions into the isotope mass balance equation:

$$\begin{aligned}\delta^{13}\text{C}_{\text{DIC}} &= m\text{HCO}_3^- \cdot (\delta^{13}\text{C}_{\text{CO}_2\text{-atm}} + \epsilon^{13}\text{C}_{\text{HCO}_3^- - \text{CO}_2}) + m\text{H}_2\text{CO}_3 \cdot (\delta^{13}\text{C}_{\text{CO}_2\text{-atm}} + \epsilon^{13}\text{C}_{\text{H}_2\text{CO}_3 - \text{CO}_2}) \\ &= 0.79(-7.5 + 9.0) + 0.21(-7.5 - 1.1) \\ &= -0.6\text{‰}\end{aligned}$$

It would seem that exchange with atmospheric CO_2 is the main control on carbonate alkalinity. Supporting evidence would be that the P_{CO_2} is very close to the atmospheric value of $10^{-3.4}$:

$$\begin{aligned}K_{\text{CO}_2} &= \frac{m\text{H}_2\text{CO}_3}{P_{\text{CO}_2}} \\ K_1 &= \frac{m\text{HCO}_3^- \cdot m\text{H}^+}{m\text{H}_2\text{CO}_3} = \frac{m\text{HCO}_3^- \cdot m\text{H}^+}{K_{\text{CO}_2} \cdot P_{\text{CO}_2}} \\ P_{\text{CO}_2} &= \frac{m\text{HCO}_3^- \cdot m\text{H}^+}{K_{\text{CO}_2} \cdot K_1} = \frac{8 \times 10^{-5} \cdot 10^{-7}}{10^{-1.34} \cdot 10^{-6.42}} \\ &= 4.6 \times 10^{-4} = 10^{-3.34}\end{aligned}$$

The P_{CO_2} of the water is very close to the atmospheric value, supporting the $\delta^{13}\text{C}$ data in concluding that CO_2 exchange with the atmosphere controls the alkalinity, rather than other processes such as oxidation of DOC in the water column or excessive photosynthesis.

If the P_{CO_2} in the above was much greater, then oxidation of DOC in the water column or from the bottom sediments would be a likely cause. Supporting evidence for such CO_2 overpressuring (P_{CO_2} greater than that at the surface) would be a more negative $\delta^{13}\text{C}_{\text{DIC}}$ value due to contributions from organics ($\delta^{13}\text{C}$ -25 to -30).

In rare situations, CO_2 underpressuring can occur. During periods of intense photosynthetic activity, algae and macrophytes in the water column consume more HCO_3^- than can be replenished by oxidation of organics or diffusion from the air. McConnaughey (1989) showed that in such situations, the P_{CO_2} in the water column may be as low as XXX and the DIC is highly depleted in ^{13}C due to kinetic effects of CO_2 diffusion from the air under non-equilibrium conditions.

Radiocarbon as a tracer of DIC

In addition to ^{13}C , the radioisotope of carbon - ^{14}C , can provide an additional constraint on the origin and evolution of DIC. Radiocarbon is produced in the upper atmosphere by cosmic radiation of ^{14}N . Oxidized to $^{14}\text{CO}_2$ it is transferred to the biosphere through photosynthesis, where it represents about 10^{-12} of the carbon in modern material. Its long half-life of 5730 years makes it useful for age dating in the late Quaternary.

However, different sources of carbon have very different radiocarbon contents. Any material of geologic age (limestones, metamorphic CO_2 , fossil fuel, bitumen, coal etc.) will have long ago lost their ^{14}C through

radioactive decay. Recently formed organic material and biogenic carbonates, on the other hand, will have levels of ^{14}C close to 100 percent modern carbon (pmC is the radiocarbon scale, with 100 pmC representing modern natural production). Vegetation formed within the past 4 decades will have values greater than 100 pmC (up to ~150 pmC) due to contributions from atmospheric testing of thermonuclear weapons in the 1960s. Today, atmospheric CO_2 has a ^{14}C content close to 120 pmC. This adds a third ^{14}C “signature” for sources of DIC.

If we look at the recharge scenarios for groundwaters in carbonate terrains presented in the last section, ^{14}C provides a useful constraint on the origin of the DIC. In the case of open system recharge, there is a thorough exchange of CO_2 between the DIC and soil atmosphere during carbonate weathering. This will impart the ^{14}C activity of the soil CO_2 on the DIC. As soil CO_2 is a product of the decay of vegetation, which is generally only a few decades old, the $a^{14}\text{C}$ of the soil CO_2 and DIC would be 100 pmC or greater.

By contrast, groundwaters that dissolve carbonate under closed system conditions will derive a significant amount of DIC from ^{14}C -free sources. From Example 5-4, half of the DIC comes from subsurface calcite. Accordingly, DIC that evolved during closed system weathering today will have $a^{14}\text{C}_{\text{DIC}} = 60$ pmC.

FURTHER READING

Garrels, R.M. and Christ, C.L., 1965. Carbonate Equilibria. Chapter 3 in: *Solutions, Minerals and Equilibria*. Freeman, Cooper & Company, San Francisco, CA, 450 pp.

Langmuir, D., 1997. Carbonate Chemistry. Chapter 6, in: *Aqueous Environmental Geochemistry*, Prentice Hall, pp. 193-230.

Drever, J., 1997. The Carbonate System and pH Control. Chapter 3 in: *The Geochemistry of Natural Waters*, Prentice-Hall, Upper Saddle River, NJ, 436 pp.

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PROBLEMS

1. A shallow groundwater has a pH of 6.4 and a measured carbonate alkalinity of 1 meq/kg. What are the activities of the DIC species, and what is the P_{CO_2} of this water?
2. How much calcite (ppm CaCO_3) will be dissolved during open system weathering of limestone in a soil with $P_{\text{CO}_2} = 10^{-2}$ and what is the final pH. Assume activities equal molalities. How much would be dissolved under closed system dissolution (hint: this will be very close to the initial carbonic acid concentration)?
3. Describe, with the relevant reactions, how recharge waters in soil developed on basalt bedrock can precipitate calcite. Note that basalts are mafic rocks dominated by calcium-rich feldspars (anorthite).
4. Determine the $\delta^{13}\text{C}$ value of the DIC in recharging groundwaters with pH 6.4 at a temperature of 15°C . How will this value change if these waters start to dissolve limestone under closed system conditions?
5. What is the P_{CO_2} of the Ahuset geothermal waters presented in Example 3-8 in Chapter 3 and suggest how it evolved?

6. Weathering experiment. Crush 3 rock types; granite, limestone and pure plagioclase feldspar to sand-size granules and weigh out 50 g of each. Add 400 ml distilled water to a 500 ml volumetric flask. Bubble a gas mixture of 5% CO₂ in air through each of the flasks, and record the stable pH. Now add the measured amounts of crushed rock to each flask, allowing the gas supply in each to mix the water and sediment in the flask. Record pH and take water samples with a syringe and plastic tubing on the following schedule: 5 m, 15 min, 2 hr, evening day 1, morning day 2, morning day 3, evening day 4, morning day 7. For each sample, take 10 mls and filter into a sample tube (labeled with experiment #, day and time) and cap. These will be analysed by Monika on Monday afternoon. With the final sample, do an alkalinity titration to determine HCO₃⁻.
1. Calculate the initial pH of the solution after equilibrating with the gas mixture and compare to the measured pH.
 2. Plot the geochemical results for the three experiments and comment on the degree of equilibrium achieved in each. Which cation best represents the weathering of the limestone, the granite and the plagioclase?
 3. Comment on the sources of the major cations in each experiment and account for their concentrations based on the minerals in these rock types.
 4. Predict the concentration of Ca²⁺ in the limestone weathering solution. How does this compare with the final value.
 5. Now run each of the water samples with WAT4 and determine the state of saturation for calcite and for the major silicate minerals (amorphous H₄SiO₄ etc.).
 6. Account for the concentrations of Al and Si in the three experiments.
 7. How does Sr²⁺ correlate with Ca²⁺? Why?
 8. Comment on the concentrations and sources of Mg²⁺ and Fe in these samples.