

Lecture: Carbonate Burial and Chemical Weathering

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Problem Statement

The mass fluxes of carbon into (degassing) and out of (burial) the surface reservoir (i.e., the ocean + atmosphere + biosphere) are large relative the surface reservoir size [28×10^{18} mols per million years vs. 2.9×10^{18} mols; Wallmann and Aloisi, 2012]. As a result, a roughly 10% imbalance between inputs and outputs would double (excess degassing) or deplete (excess burial) the mass of C in the surface reservoir in about 1 millions years with clear implications for Earth's climate. Due to the sensitivity of the geologic C cycle to imbalance, many researchers have argued for a stabilizing negative feedback between input and output fluxes [see Berner and Caldeira, 1997, Broecker and Sanyal, 1998]. Since the time rate of change in the partial pressure of CO_2 in the atmosphere ($p\text{CO}_2$) should scale with magnitude of the C cycle imbalance and atmospheric CO_2 is a greenhouse gas that modulates Earth's temperature and hydrologic cycle, negative C cycle feedbacks are often presumed to operate via changes in climatic conditions [Walker et al., 1981, Berner et al., 1983]. While surface reservoirs export C both as carbonate minerals and organic matter, carbon isotope mass balance constraints [Schidlowski, 1988] suggest that the burial of carbonate minerals has been the dominant mode of C export over most of Earth's history (Figure 1). As such, negative C cycle feedbacks are presumed to operate through the inorganic C cycle [Walker et al., 1981, Berner et al., 1983, Broecker and Sanyal, 1998].

Carbonate Burial

The production carbonate minerals (e.g., CaCO_3) in the ocean and their burial in marine sediments is responsible for the transfer of large masses of C out of surface reservoirs. To precipitate and preserve CaCO_3 , seawater must be *super-saturated* with respect to carbonate phases (i.e., there must be a thermodynamic driving force for the reaction). To evaluate the saturation state of the ocean with respect to CaCO_3 phases, we can start by writing an equation describing the solubility of calcite¹. The equilibrium constant for this reaction is known as the solubility product (K_{sp}). Note that, by convention, the activity of a solid phase is equal to 1.

The saturation state (Ω) of the ocean with respect to calcite (or any other mineral phase) is based on the ratio of the activity product of the constituent ions in the environment versus the solubility product². If the product of the activities of calcium and carbonate ions in seawater exceeds the solubility product ($\Omega > 1$), then there is a thermodynamic driving force for carbonate precipitation.

While the $\Omega > 1$ is essential for carbonate burial, the spontaneous, abiotic formation of carbonates is inhibited in seawater at typical temperatures and salinities until $\Omega \approx 20$ [Morse and He, 1993]. Bi-

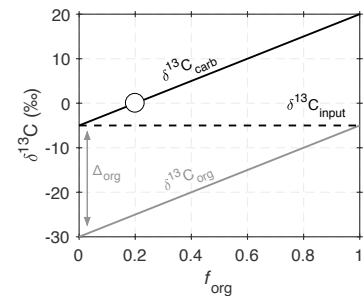


Figure 1: Steady-state C isotope mass balance. The near zero $\delta^{13}\text{C}$ of marine carbonates over geologic history implies that a majority ($\sim 80\%$) of C leaves surface reservoirs as a carbonate mineral.

¹ Calcite Solubility
 $\text{CaCO}_3(\text{s}) \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$
 $K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$

² Calcite Saturation
 $\Omega = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{sp}}$

ological activity significantly lowers this threshold for carbonate precipitation [e.g., coral ecosystems can precipitate CaCO_3 at Ω as low as 2; Langdon et al., 2000].

In abiotic [Shiraki and Brantley, 1995] and some biotic systems [Langdon et al., 2000], the rate at which CaCO_3 precipitates increases with the degree of super-saturation (Figure 2). This saturation-state dependence implies that, if more calcium and carbonate ions are added to the ocean, then they will be more efficiently removed. So, total CaCO_3 burial fluxes should adjust to balance the input fluxes of calcium and carbonate ions. To this same effect, biota in the modern ocean “over-produce” CaCO_3 relative to input fluxes as their activity is, presumably, controlled more by nutrient supply than ocean carbonate chemistry [Broecker, 1971]. Ultimately, input/output balance is achieved through the dissolution of CaCO_3 on the sea floor, which also depends on seawater saturation state [Broecker, 1971].

Silicate Weathering

The chemical weathering of the continents (and sea floor) transfers calcium and carbonate ions to the ocean. Since the supply of calcium and carbonate ions from the dissolution of CaCO_3 is exactly balanced by their removal through CaCO_3 precipitation/burial, carbonate weathering can be ignored when considering the *net* removal of carbon from surface reservoirs.

The proton-promoted dissolution of silicate minerals generates dissolved calcium as well as other alkaline (Na^+ , K^+) and alkaline earth (Mg^{2+}) cations ³. The dissolution of CO_2 into natural waters can supply the protons necessary to drive silicate weathering, which, *effectively*, leads to the generation of carbonate ions ⁴.

Reaction Kinetics

In laboratory experiments, the rates of silicate mineral dissolution (mols released per unit surface area per time) depend on factors such as temperature, pH, mineral chemistry, and solution chemistry [Lasaga et al., 1994]. The temperature (T) dependence of laboratory weathering reactions is often described using the Arrhenius relationship ⁵. This relationship indicates that dissolution rates increase exponentially with increasing temperature. Since surface temperatures increase with increasing atmospheric $p\text{CO}_2$, a temperature dependence of weathering rates constitutes a possible negative C cycle feedback [Walker et al., 1981]. However, an Arrhenius temperature dependence is not always apparent in field data (Figure 3).

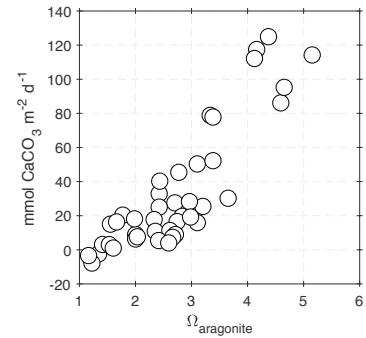
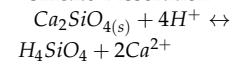
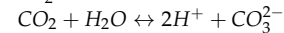


Figure 2: Dependence of coral community aragonite precipitation rates on solution saturation state in an experimental system [Langdon et al., 2000]. Increases in precipitation rates with saturation state implies marine carbonate burial can adjust to supply of calcium and carbonate ion.

³ Silicate Dissolution



⁴ CO_2 dissolution



⁵ Arrhenius equation

$$k = A e^{-E_a/RT}$$

where k is a rate constant (mols released $\text{m}^{-2} \text{ t}^{-1}$), A is a pre-factor (units of k), R is the gas constant, and E_a is the activation energy (units of RT)

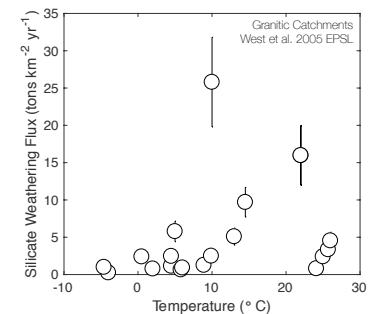


Figure 3: Temperature dependence of weathering in granitic catchments. Scatter in the data imply that an Arrhenius temperature dependence alone does not explain the variability in weathering fluxes at Earth’s surface today.

Environmental “limits” to kinetics

As dissolution progresses, the fluid phase will approach saturation with respect to the dissolving phase. By definition, *net* dissolution rates are zero at equilibrium (i.e., the reaction stops). Reaction rates also slow down as solutions *approach* equilibrium [Lasaga et al., 1994].

The fact that silicate dissolution will stop when solutions reach equilibrium means that the timescale over which waters react with rocks at Earth’s surface can control weathering fluxes (Figure 4). This competition between fluid transport, which controls water-rock interaction times, and reactions kinetics is a classic chemical engineering problem. It can be evaluated by considering two timescales: the time required for fluids to reach equilibrium with respect to the dissolving phase (τ_{eq} ; proportional to $1/k_{sil}$) and the duration of time over which the reaction occurs (τ_w ; proportional to fluid fluxes).

If the contact time between water and rock (τ_w) is much *greater* than τ_{eq} , then changes in the reaction kinetics (e.g., due to a temperature dependence of k_{sil}) will not have an effect on the total weathering flux because the system is already at equilibrium. However, under these conditions, changing the fluid flux (Q) can increase the weathering flux by equilibrating more fluid per unit time. This offers the potential for an alternative negative C cycle feedback that operates through the intensification of the hydrological cycle [Maher and Chamberlain, 2014].

If the contact time between water and rock (τ_w) is much *shorter* than τ_{eq} , then changes in the reaction kinetics will affect the total weathering flux since the system is far from equilibrium. Since the fluid residence time is coupled to the fluid flux, increasing Q when $\tau_w \ll \tau_{eq}$ likely won’t change weathering fluxes. In chemical engineering parlance, the ratio of a reaction timescale (τ_{eq}) to a transport timescale (τ_w) is referred to as a *Damköhler Number*.

Environmental controls on mineral supply

As silicate weathering reactions progress, the mass of un-weathered minerals remaining decreases leading to an overall decrease in the weathering flux. Without the re-supply of fresh minerals, weathering fluxes will ultimately drop to zero. Tectonic uplift (U ; $m^3 \text{ yr}^{-1} \text{ m}^{-2}$) brings fresh rock to the surface and creates topography. This topography is destroyed by weathering (W) as well as erosion (E ; Figure 6), which is the physical transport of un-weathered materials and solid-phase weathering products. The sum of weathering and erosion is termed denudation ($D = W + E$). At topographic steady-state (i.e., when the elevation of the land surface is constant in time), the mass of rock added by tectonic uplift is balanced by the mass exported

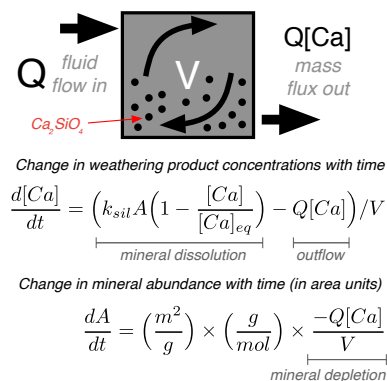


Figure 4: A well-mixed chemical reactor. $[Ca]$ is the concentration of weathering products, $[Ca]_{eq}$ is the equilibrium concentration of reaction products, k_{sil} is the dissolution rate constant under a given set of physico-chemical conditions ($\text{mols } m^{-2} \text{ t}^{-1}$), A is the available mineral surface area (m^2), Q is the fluid flux, and V is the reactor volume. Depending upon the ratio of reactor residence time (Q/V ; τ_w) to the τ_{eq} , concentrations will be either at or below equilibrium. At equilibrium, mass fluxes are controlled by Q . Far from equilibrium, mass fluxes are controlled by $k_{sil} A$. Overtime, the mass of mineral present in the reactor will become depleted due to repeated flushing with reactive fluid.

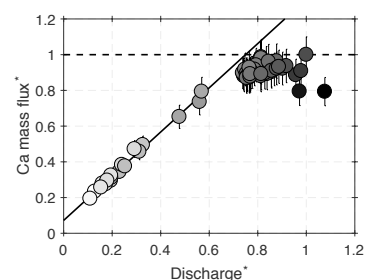


Figure 5: Effect of hydrology on Ca fluxes in the Andes Mountains [Torres et al., 2015]. Darker points correspond to lower dissolved Ca concentrations. Both discharge and mass flux values are relative to the maximum observed mass flux of the system. While nature is not a “well-mixed” reactor, natural systems *do* show similar behavior.

from the surface by denudation ($D = U$).

There should be some depth (z) at which weathering reactions commence, which defines the extent of the “weathering zone” (Figure 6). At steady-state, the amount of time available for weathering (rock residence time; τ_r) is the ratio of the weathering zone depth (z ; m) to the uplift rate (U ; m yr^{-1}).

Lumping together all of the effects of available surface area, temperature, and the competition between fluid flow and chemical equilibrium, silicate minerals can be considered to dissolve at some rate (K ; yr^{-1}), so the mass lost via weathering per unit time should be proportional to the concentration (C) of minerals present within the weathering zone. Under these conditions⁶, which are termed first-order kinetics, the time (τ_{sil}) for weathering to reduce mineral concentrations by a factor of e relative to the parent material is equal to the inverse of the rate constant ($1/K$).

When τ_r is much greater than τ_{sil} , all material exported from the weathering zone will be completely weathered. This condition is termed “supply-limited” [Riebe et al., 2004] or “transport-limited” [Carson and Kirkby, 1972, Stallard and Edmond, 1983] weathering because weathering fluxes will be proportional to the supply (or transport) of fresh material by uplift (Figure 7). Under supply-limitation, changes in weathering kinetics do not necessarily lead to changes in weathering fluxes [Riebe et al., 2001, West et al., 2005].

WHEN τ_r is close τ_{sil} , un-weathered minerals will be exported from the weathering zone. This condition is termed “kinetically-limited” [West et al., 2005] or “weathering-limited” [Carson and Kirkby, 1972, Stallard and Edmond, 1983] because, at a given uplift rate, weathering fluxes may vary with the overall kinetics of weathering (i.e., K ; Figure 7).

A RELATED concept is *weathering intensity*, which can be defined as the ratio of the weathering flux to the denudation flux (W/D). Supply-limited weathering should result in a constant weathering intensity. Kinetically-limited weathering will produce lower, but more variable weathering intensities. Note that most stable isotopic proxies for chemical weathering (e.g., Li, Si, and Ge isotopes) trace weathering intensity and not weathering fluxes directly.

SINCE different minerals weather at different rates, co-existing minerals in a rock can weather under supply- and kinetically-limited conditions at the same time.

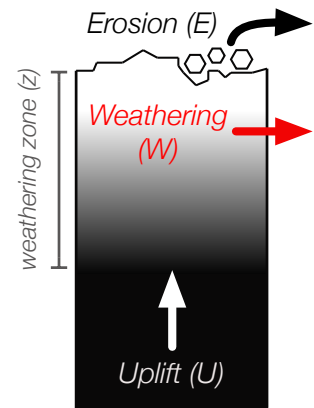


Figure 6: Weathering zone schematic. “Fresh” minerals are brought to the surface by uplift and removed by chemical weathering and/or physical erosion. The proportion of the uplift flux that gets chemically weathering depends on the ratio of the rock residence time (τ_r) to the time required for weathering to deplete the available mineral stock (τ_{sil}).

$${}^6 \frac{dC}{dt} = -K(C)$$

$$C(t) = C_0 e^{-Kt}$$

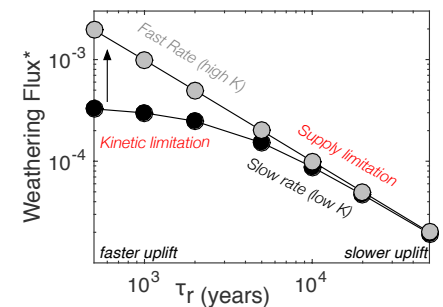


Figure 7: End-member weathering conditions. Weathering flux* is equal to $U \times z \times (1 - (C/C_i))$. When τ_r is long (low uplift rate), all weather-able minerals are consumed and the total weathering flux scales with the uplift rate (supply-limited). When τ_r is short (high uplift rate), un-weathered minerals are exported from the weathering zone and the total weathering flux depends on the reaction kinetics (kinetically-limited). Model from Li et al. [2014]

Strength of the Weathering Feedback

In the discussion above, we identified multiple mechanisms for a climatic control on the fluxes of calcium and carbonate ion to the ocean. Climate can control the kinetics of weathering directly through temperature [e.g., Walker et al., 1981] or indirectly through fluid fluxes [e.g., Maher and Chamberlain, 2014]. Note that, under a warmer climate state (higher $p\text{CO}_2$), the atmosphere can hold more water vapor leading to an intensified hydrological cycle [Held and Soden, 2006].

The *strength* of the climatic control on weathering (i.e., the proportional change in the weathering flux for a given change in climate) depends, in part, on the supply of fresh minerals to Earth's surface by tectonic uplift, which dictates the timescales over which weathering reactions occur and the overall efficiency of chemical weathering (i.e., W/D). Increased tectonic activity (i.e., more mineral supply), should lead to an increase in the strength of the weathering feedback [i.e., larger portion of land surface kinetically-limited; West et al., 2005, Maher and Chamberlain, 2014]. If chemical weathering was 100% efficient globally (i.e., $W/D = 1$), then there would be no weathering feedback as any increase in weathering *rates* would not generate a increase in weathering *fluxes*.

LET'S ASSUMING THAT, integrated across the globe, weathering fluxes are proportional to atmospheric $p\text{CO}_2$ (with a constant of proportionality \bar{K} that captures all of the effects of temperature, fluid flow, and uplift). Under these conditions, the steady-state atmospheric $p\text{CO}_2$ is equal to the $p\text{CO}_2$ required for carbonate burial to keep pace with degassing inputs for the available amount of mineral surface area ⁷. This relationship suggest that, changes in \bar{K} will *force* changes in atmospheric $p\text{CO}_2$ independent of the degassing rate. Changes in tectonic uplift might increase \bar{K} as some environments will shift to kinetically-limited conditions and global mineral supply rates will increase [i.e., mountain uplift may drive a decrease in $p\text{CO}_2$ Raymo et al., 1988]. Changes in \bar{K} might also be caused by changing the proportion of mafic (more reactive) versus felsic (less reactive) lithologies at Earth's surface [Bluth and Kump, 1994]. Taken all together, our planet's "thermostat" may have multiple "set points" [West, 2012, Maher and Chamberlain, 2014].

$${}^7 \frac{dM}{dt} = P - (\bar{K} \times \alpha M)$$

where α represents the portion of surface carbon (M) partitioned into the atmosphere (i.e., $p\text{CO}_2 = \alpha M$).
When $\frac{dM}{dt} = 0$, $p\text{CO}_2 = P/\bar{K}$

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