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Abstract  Chemical weathering is one of the major processes interacting with climate and tectonics to form clays, supply nutrients to soil microorganisms and plants, and sequester atmospheric CO₂. Hydrology and dissolution kinetics have been emphasized as factors controlling chemical weathering rates. However, the interaction between hydrology and transport of dissolved inorganic carbon (DIC) in controlling weathering has received less attention. In this paper, we present an analytical model that couples subsurface water and chemical molar balance equations to analyze the roles of hydrology and DIC transport on chemical weathering. The balance equations form a dynamical system that fully determines the dynamics of the weathering zone chemistry as forced by the transport of DIC. The model is formulated specifically for the silicate mineral albite, but it can be extended to other minerals, and is studied as a function of percolation rate and water transit time. Three weathering regimes are elucidated. For very small or large values of transit time, the weathering is limited by reaction kinetics or transport, respectively. For intermediate values, the system is transport controlled and is sensitive to transit time. We apply the model to a series of watersheds for which we estimate transit times and identify the type of weathering regime. The results suggest that hydrologic transport of DIC may be as important as reaction kinetics and dilution in determining chemical weathering rates.

1. Introduction

Chemical weathering takes part in the complex system of feedbacks between climate and geochemical processes regulating the carbon cycle (Berner, 1994), soil acidification (Sverdrup & Warfvinge, 1988; Whitfield et al., 2006), soil clay formation (Eberl et al., 1984; Sposito, 2008) and landscape development (Dixon et al., 2009; Mudd & Furbish, 2004; Rasmussen et al., 2011). Chemical weathering of silicate minerals is also one of the major processes that modulates climate through consumption of atmospheric carbon dioxide (CO₂) (Garrels, 1983; Stumm & Morgan, 1995; Urey, 1952; Walker et al., 1981), as dissolved inorganic carbon is the main chemical driver of silicate mineral dissolution reactions. Over geologic timescales the consumption of CO₂ by silicate weathering regulates atmospheric CO₂ concentration (Holland et al., 1986), whereas over much smaller timescales, the balance of soil CO₂ production by root and microbial respiration (Richter & Markewitz, 1995) and mineral dissolution controls soil acidification (Markewitz et al., 1998; Richter & Markewitz, 2001). Therefore, understanding the long-term evolution of soils and climate, relevant to sustainability of the critical zone, necessitates a quantitative description that links the production, transport, and chemical fate of CO₂ in the subsurface (van Haren et al., 2017) to chemical weathering rates.

Temperature and the hydrologic cycle are the two main climatic factors that affect weathering rates. The former is extremely important as an increase in temperature accelerates weathering reaction rates. On the other hand, CO₂ sequestered through weathering regulates atmospheric CO₂, thus imposing a negative feedback on temperature (Kump et al., 2000; Walker et al., 1981). In parallel, water influences mineral weathering by participating in the chemical reactions as a reactant as well as by transporting [H⁺] ions and other chemical species from the surface to subsurface weathering sites (Kessler & Harvey, 2001; Stumm & Morgan, 1995). The role of water has been evaluated mostly in terms of rainfall (Dixon et al., 2016; Gislason et al., 2009; White & Blum, 1995; West et al., 2005; Riebe et al., 2004), its residence time (Maher, 2010; Maher & Chamberlain, 2014; Li et al., 2014), and hydraulic conductivity of soils (Gabet et al., 2006).
Chemical weathering also interacts with physical erosion and tectonic processes during soil formation (Eberl et al., 1984). While tectonic uplift supplies fresh minerals to the soil and chemical weathering alters their compositions forming clays, physical erosion transports weathered material to rivers and ultimately the ocean. When the weathering rate is limited by the supply of fresh minerals (Hilley et al., 2010; Oliva et al., 2003), its sensitivity to climatic factors is reduced (Li et al., 2014; Riebe et al., 2004) and the tectonic uplift becomes the major control (Jacobson & Blum, 2003; Millot et al., 2002). Some authors have emphasized that supply-limited conditions are determined when the mineral reaction time (inverse of the kinetic constant) is much shorter than the rock residence time in the regolith (Hilley et al., 2010; Li et al., 2014; Maher, 2010).

Along with the estimation of weathering rates based on field observations (Brimhall & Dietrich, 1987; Dixon et al., 2016; Maher et al., 2009; West et al., 2005; White et al., 2008; White & Blum, 1995; White & Brantley, 2003; Riebe et al., 2003, 2004), numerous detailed numerical models have been developed to couple geochemical processes to water dynamics and temperature in unsaturated and saturated media (Cederberg et al., 1985; Mangold & Tsang, 1991; Nielsen et al., 1986; Saaltink et al., 2004; Samson et al., 2000; Suarez & Simunek, 1997; Steefel & Lasaga, 1994; Yeh & Tripathi, 1991). These typically consider numerical solutions of Richards’ or groundwater equations coupled with partial differential equations describing the reactive transport of the chemical species. While these models provide a detailed space-time description of the weathering process, the wide range of timescales involved in the various processes taking place in the critical zone (Brantley, 2008) makes these complex numerical approaches unsuitable for long-term predictions as well as for theoretical analysis of the interplay between the main system variables under different environmental scenarios. On the contrary, simpler models that have been proposed do not account for external climatic forcings (Gabet et al., 2006) or focus only on the role of tectonic processes (Gabet & Mudd, 2009; Hilley et al., 2010; Li et al., 2014). To our knowledge, no model has yet considered consistently the dissolution and transport of CO₂ and its dependence on surface hydrological processes in relation to the dynamics of the weathering process. There is then a need for analytical models to predict the role of climate, hydrology, and CO₂ dissolution and transport on chemical weathering, which are amenable to theoretical analysis and upscaling in space and time.

Toward this goal, in the present study we develop a model based on molar balance equations for the chemical species in the weathering zone. Aiming to isolate the effect of hydrology, we assume that the reaction is not limited by the supply of fresh mineral by tectonic processes, and that the products of the reactions are removed only by water transport. The model is thus more applicable to regions where the tectonic activity is fast compared to the weathering reactions (e.g., Li et al., 2014; Riebe et al., 2004). The dissolution and speciation of CO₂ is assumed to be at equilibrium at any given time, whereas the weathering reaction is described through a kinetic rate law (Lasaga et al., 1994; Maher et al., 2009). For the sake of simplicity, we neglect the ion interactions, which take place at high solute concentrations (high ionic strength), and neglect the effect of biological activity and temperature on the kinetic constant. Similarly, we do not take into account the presence of ion-exchange reactions. We set the balance equations in a way that can be generally formulated for multiple minerals subject to different weathering reactions, although here we consider only the weathering of albite to kaolinite. Using this model we explore the effects of the percolation rate, CO₂ dissolution and transport, and the water transit time on the weathering rate dynamics. The model reveals that the percolation flux impacts the weathering reaction mainly by transporting dissolved inorganic carbon, while water transit time is an indicator of dilutive effects.

The remainder of the manuscript is organized as follows. The model is described in section 2, and steady state solutions are presented as a function of the percolation rate in section 3 and as a function of the water transit time in section 4. Section 5 discusses the role of nonlinear expressions for the groundwater discharge. In section 6 a comparison with measured weathering rates is introduced. The results are summarized in section 7.

2. Model Description

Consider a soil regolith subdivided into a solum, which includes the O, A, E, and B soil horizons, and the underlying layer of saprolite (fractured parent material) on top of a consolidated bedrock formation. In this schematic representation of the regolith, see Figure 1, the bedrock is assumed impervious and the water table is located within the unconsolidated layer. Focusing on the weathering of the parent material, the weathering zone can be interpreted as the volume delimited by the bedrock at the bottom and the water table at the top. The spatially implicit model described below is derived from spatial integration of reactive transport...
equations and couples the water table (i.e., weathering zone depth) and chemical dynamics in this weathering zone. Because of these simplifying assumptions, the model is more suitable to large regions, for which one can more safely consider averages over the spatial complexity of topography, mineralogy, rainfall, and other factors. Because the present analysis focuses on time scales of soil development, average values of the hydrological and chemical parameters and simple phenomenological expressions are used.

2.1. Leakage Chemistry

Water percolating from the surface soil layers influences the weathering reaction by transporting dissolved inorganic carbon to the weathering zone. The amount of CO₂ dissolved in the percolating water depends on the equilibrium with the partial pressure, \(P_{CO_2}\), in the top soil layer (Kessler & Harvey, 2001). Due to root and microbial respiration, \(P_{CO_2}\) is generally higher than the reference value in the atmosphere, \(P_0\). As shown in Daly et al. (2008), the daily dynamics of CO₂ are characterized by instantaneous jumps induced by rainfall events and linear decay between rainfall events.

Based on these findings, we assume that the partial pressure of CO₂ in the soil gas is empirically linked to the percolation rate, \(L\),

\[
P_{CO_2} = P_0 + K(L)L,
\]

where the proportionality coefficient \(K(L)\) can be, in general, a function of \(L\). The functional form of \(K(L)\) accounts for processes enhancing or inhibiting the production of CO₂ and needs to be determined experimentally. The analysis shown here is conducted following the observations at the Duke Forest (Daly et al., 2008), for which \(K(L)\) is a constant. As more data become available for other conditions, different assumptions regarding \(K(L)\) can be readily accommodated within the present framework.

The model accounts for dissolution and speciation of CO₂ in water, which at any given time are assumed to be in thermodynamic equilibrium. Therefore, Henry’s Law determines the concentration of the total analytical concentration of dissolved CO₂, \(\left[H_2CO_3^*\right] = CO_2(aq) + \left[H_2CO_3\right]\),

\[
\left[H_2CO_3^*\right] = K_HPCO_2,
\]

where \(K_H\) is the Henry’s law constant. The equilibrium constants, \(K_1\) and \(K_2\), then determine the deprotonation of \(H_2CO_3^*\) that yields \(HCO_3^-\) and \(CO_3^{2-}\) (Kessler & Harvey, 2001; Lasaga, 1984),

\[
\begin{align*}
H_2CO_3^* & \rightleftharpoons H^+ + HCO_3^- \\
HCO_3^- & \rightleftharpoons H^+ + CO_3^{2-},
\end{align*}
\]

while \(K_w\) regulates the self-ionization of water,

\[
H_2O \rightleftharpoons H^+ + OH^-.
\]

Pertaining to the release of \([H^+]\) ions, the reactions (3) and (4) are functions of pH. Defining the sum of \(\left[H_2CO_3^*\right]\), \(\left[HCO_3^-\right]\) and \(\left[CO_3^{2-}\right]\) as the total dissolved inorganic carbon \(C_T\) (DIC), each carbonate species can be expressed as fractions of \(C_T\)

\[
\begin{align*}
\alpha_0 &= \frac{\left[H_2CO_3^*\right]}{C_T} \\
\alpha_1 &= \frac{\left[HCO_3^-\right]}{C_T} \\
\alpha_2 &= \frac{\left[CO_3^{2-}\right]}{C_T},
\end{align*}
\]

where the ionization fractions \(\alpha_0, \alpha_1,\) and \(\alpha_2\) are explicit functions of \([H^+]\), reflecting the dependence of the carbonate system on pH.
Figure 2. Chemical composition of the percolating water as a function of the percolation rate \( L \) and assumed root zone alkalinity \( A_L \) computed from equations (1), (2), and (9). The inset shows the resulting \( C_T \) as a function of the percolation rate, for \( A_L = 1 \) (eq/m³). Parameters: \( P_0 = 10^{-3.5} \) atm, \( K(L) = K = 10^{-1} \) atm d/m, equilibrium constants \( K_1 = 10^{-6.3} \) mol/m³ and \( K_2 = 10^{-10.3} \) mol/m³, and Henry's constant \( K_H = 33.9 \) (mol/m³/atm).

Alkalinity is defined as

\[
A = [ \text{HCO}_3^- ] + 2 [ \text{CO}_3^{2-} ] - [ \text{H}^+ ] + [ \text{OH}^- ]. \tag{8}
\]

and by introducing (6), (7), and (4) into (8), we obtain (Stumm & Morgan, 1995)

\[
A = C_T (\alpha_1 + 2\alpha_2) + K_w / [ \text{H}^+ ] - [ \text{H}^+] \tag{9}
\]

which links \( A \), \( C_T \), and pH. In order to compute the chemical composition of the percolating water, we fix the value of alkalinity \( A^L \) (we use the superscript \( L \) to indicate that the value refers to percolation) and then for a given percolation rate \( L \), we calculate \( C_T \) and \([ \text{H}^+] \) from (1), (2), (5), and (9) (Stumm & Morgan, 1995). The choice to fix \( A^L \) is motivated by the fact that the addition of \( \text{CO}_2 \) into the system changes the value of \( C_T \) and pH, without altering \( A \).

As the percolation rate increases, \( P_{\text{CO}_2} \) and \( C_T \) rise, so that more \( \text{H}^+ \) ions are released and the pH decreases (Figure 2). The three related quantities \( L \), \( C_T \), and \( A^L \), and intrinsically the pH, thus represent the external forcing to the weathering zone that together with other weathering reactants or products percolating from upper soil layers perturb the weathering reaction during its evolution toward equilibrium.

2.2. The Weathering Zone

The weathering zone is considered as a control volume that is filled by the percolation \( L \) and releases water through the loss term \( Q \). The water balance for the weathering zone of height \( h \) is expressed as

\[
n \frac{dh}{dt} = L(t) - Q(t), \tag{10}
\]

where \( n \) is the porosity. The percolation rate \( L \) represents the portion of water that reaches the weathering sites in the deeper soil layers, can be characterized by intraseasonal to interannual variability, and is considered here as the external hydrologic forcing. The discharge \( Q \) depends on the complex and heterogeneous structure of the groundwater system so that various relationships with the water storage, \( Q = Q(h) \), may be assumed. Here for the sake of simplicity we adopt the following relationship (Ceola et al., 2010; McDonnell, 2013)

\[
Q = k_Q h^\beta, \tag{11}
\]

where \( k_Q \) is the specific output rate and the exponent \( \beta \) determines the degree of nonlinearity. When more detailed information is available, (11) can be replaced with more suitable functions without affecting the development of the rest of the theory. Equation (10) is spatially implicit in that no spatial variability in either the vertical or horizontal directions is considered.

The weathering zone chemistry includes the DIC system and the weathering products. The DIC system at any given time is assumed to reach equilibrium very fast and thus, analogous to the chemistry of the percolating
water, is determined by the equilibrium reactions (3) and the self-ionization of water (4). On the contrary, the weathering reaction proceeds much more slowly, thus requiring a kinetic description of the reaction for the specific mineral being weathered. Given the important role of silicate weathering in global climate and the availability of data for feldspar minerals (e.g., Chou & Wollast, 1985; White, 1995; White & Brantley, 2003; White et al., 2008; Maher et al., 2009), we formulate the model for the weathering of albite (NaAlSiO₄) with precipitation of kaolinite (Al₂Si₂O₅(OH)₄). Specifically, albite is a plagioclase mineral that occurs mostly in igneous rocks (e.g., granite) and also in metamorphic formations. Being one of the prevailing minerals found in parent materials (e.g., the granitic gneiss at the Calhoun CZ observatory), albite often takes part in soil formation. Considering the following congruent reaction for dissolution of albite,

\[ 4\text{H}_2\text{CO}_3 + \text{NaAlSi}_3\text{O}_8 + 4\text{H}_2\text{O} \rightleftharpoons \text{Al}^{3+} + \text{Na}^+ + 4\text{HCO}_3^- + 3\text{H}_2\text{SiO}_4. \] (12)

and the one for precipitation of kaolinite,

\[ \text{Al}^{3+} + \text{H}_2\text{SiO}_4 + \frac{1}{2}\text{H}_2\text{O} + 3\text{HCO}_3^- \rightleftharpoons \frac{1}{2}\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 3\text{H}_2\text{CO}_3 + 3\text{H}_2\text{SiO}_4. \] (13)

the overall representative incongruent reaction for albite weathering can be written as

\[ \text{H}_2\text{CO}_3 + \text{NaAlSi}_3\text{O}_8 + \frac{9}{2}\text{H}_2\text{O} \rightleftharpoons \frac{1}{2}\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Na}^+ + \text{HCO}_3^- + 2\text{H}_2\text{SiO}_4. \] (14)

In the above reactions, the dissolution of albite is the rate-limiting step, while the precipitation of kaolinite is relatively fast and can be considered an equilibrium reaction (e.g., Li et al., 2014).

The time evolution of the mass per unit ground area of weathering products and carbonate species is then described by the set of ordinary differential equations

\[ n \frac{d}{dt} \frac{[\text{H}_2\text{CO}_3^\ddagger]}{[\text{Na}^+]} = L_{\text{H}_2\text{CO}_3} - Q_{\text{H}_2\text{CO}_3} - R_2 - hW, \] (15)

\[ n \frac{d}{dt} \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{O}]} = L_{\text{HCO}_3^\ddagger} - Q_{\text{HCO}_3} + R_2 - R_3 + hW, \] (16)

\[ n \frac{d}{dt} \frac{[\text{CO}_2^-]}{[\text{H}_2\text{O}]} = L_{\text{CO}_2^\ddagger} - Q_{\text{CO}_2^\ddagger} + R_3, \] (17)

\[ n \frac{d}{dt} \frac{[\text{H}^+]}{[\text{Na}^+]} = L_{\text{H}^+} - Q_{\text{H}^+} + R_2 + R_3 + R_4, \] (18)

\[ n \frac{d}{dt} \frac{[\text{OH}^-]}{[\text{H}_2\text{SiO}_4]} = L_{\text{OH}^-} - Q_{\text{OH}^-} + R_4, \] (19)

\[ n \frac{d}{dt} \frac{[\text{Na}^+]}{[\text{Na}^+]} = L_{\text{Na}^+} - Q_{\text{Na}^+} + hW, \] (20)

\[ n \frac{d}{dt} \frac{[\text{H}_2\text{SiO}_4]}{[\text{H}_2\text{SiO}_4]} = L_{\text{H}_2\text{SiO}_4} - Q_{\text{H}_2\text{SiO}_4} + 2hW. \] (21)

Equations (15)–(21) are obtained by spatially integrating the chemical transport equations (e.g., see Cederberg et al., 1985; Nielsen et al., 1986) over the weathering zone. Derived from such integration, \( L \) and \( Q \) represent the total hydrologic transport component, while the \( R \)'s and \( h \cdot W \) are the volumetric reaction rates for the equilibrium DIC system (equations (3) and (4)) and the weathering process (reaction (14)), respectively. Note that the volumetric weathering rate is assumed to scale with the weathering zone depth, that is, \( h \cdot W \), which accounts for the fact that the surface area exposed to the reaction increases with the depth of saprolite that is saturated. The terms \( L_{\text{Na}^+} \) and \( L_{\text{H}_2\text{SiO}_4} \), respectively, account for \( \text{Na}^+ \) and \( \text{H}_2\text{SiO}_4 \) percolating from upper soil layers while the outflows of solutes can be expressed as the product of the discharge \( Q \) and their concentrations. For example, the outflow of \( \text{Na}^+ \) can be computed as \( Q_{\text{Na}^+} = Q \cdot [\text{Na}^+] \).
To close the system (15)–(21), a phenomenological equation is needed for $W$. We compute the weathering rate $W$ for the overall congruent reaction (14) through the expression (see Appendix A for the derivation) (Maher et al., 2009; Maher, 2010; Lasaga et al., 1994; Lasaga, 1998),

$$ W = w_{\text{max}} \left[ 1 - \frac{\Theta}{K_{\text{eq}}} \right], \quad (22) $$

where $w_{\text{max}} = K_{\text{alb}}\rho_{\text{alb}}\alpha_{\text{alb}}$ (mol/m²/d) represents the product of the kinetic parameters, namely, the kinetic rate constant $K_{\text{alb}}$ (mol/m²/d), the albite density $\rho_{\text{alb}}$ (g/m³), and the albite specific surface area $\alpha_{\text{alb}}$ (m²/g). The ion activity product is given by

$$ \Theta = \left[ \frac{\text{Na}^+}{} \right] \left[ \frac{\text{HCO}_3^-}{} \right] \left[ \frac{\text{H}_2\text{SiO}_4^2-}{\text{H}_2\text{CO}_3^+} \right]. \quad (23) $$

Using equations (5) and (6), one can write also

$$ \Theta = \frac{a_1}{a_0} \left[ \frac{\text{Na}^+}{} \right] \left[ \frac{\text{H}_2\text{SiO}_4^2-}{} \right]. \quad (24) $$

Given the first dissociation constant of silicic acid, $pK_a = 9.8$, at pH $= 8$, for example, $[\text{H}_2\text{SiO}_4]$ is already much greater than $[\text{H}_4\text{SiO}_4]$; that is, $[\text{H}_2\text{SiO}_4] \approx 10^2 \cdot [\text{H}_4\text{SiO}_4]$. We therefore proceed by assuming that the deprotonation of the silicic acid $\text{H}_2\text{SiO}_4$ is negligible, meaning that the total dissolved silicon $\Sigma_{\text{Si}} \approx [\text{H}_2\text{SiO}_4]$.

Equation (16) assumes the activity coefficients are equal to 1, thus neglecting the interactions between solutes typical of high ionic strength. Expression (22) however captures the key dynamics of precipitation-dissolution processes (Drever & Clow, 1995). The use of more complex expressions (Chou & Wollast, 1985; Maher et al., 2009; Maher, 2010; Lasaga et al., 1994; Lasaga, 1998) would require a more detailed parameterization that is not available when large regions are considered.

Since $C_T$ and $A$, as defined, are conservative with respect to the equilibrium reactions, equations (15)–(21) can be further condensed by algebraic manipulation that eliminates the $R_i$'s and yields

$$ \frac{dC_T}{dt} = \frac{1}{nh} \left[ L \left( C_T^i - C_T \right) \right], \quad (25) $$

$$ \frac{dA}{dt} = \frac{1}{nh} \left[ L \left( A^i - A \right) + hW \left( [H^+] \cdot [\text{Na}^+] \cdot [\Sigma_{\text{Si}}] \right) \right]. \quad (26) $$

$$ \frac{d[\text{Na}^+]}{dt} = \frac{1}{nh} \left[ L \left( [\text{Na}^+]^i - [\text{Na}^+] \right) + hW \left( [H^+] \cdot [\text{Na}^+] \cdot [\Sigma_{\text{Si}}] \right) \right], \quad (27) $$

$$ \frac{d\Sigma_{\text{Si}}}{dt} = \frac{1}{nh} \left[ L \left( \Sigma_{\text{Si}}^i - \Sigma_{\text{Si}} \right) + 2hW \left( [H^+] \cdot [\text{Na}^+] \cdot [\Sigma_{\text{Si}}] \right) \right]. \quad (28) $$

Equations (10) and (25)–(28) form a nonlinear dynamical system that fully determines the weathering of albite in the weathering zone as forced by the $C_T$ and its speciation transported by percolation. The system is constrained by the alkalinity equation (9), since $[H^+]$, which is necessary for the calculation of $W$, is computed from $A$ and $C_T$. Due to the nonlinearity imposed by $W$ and the alkalinity constraint (9), the variables $[\text{Na}^+]$, $\Sigma_{\text{Si}}$, and $A$ are calculated implicitly. This new framework is compact and explicitly accounts for the transport of DIC, the speciation of $[\text{H}_2\text{CO}_3^+]$, and its effects on chemical weathering.

### 3. Steady State Solution

The system (10) and (25)–(28) is here analyzed under deterministic, steady state conditions with a constant percolation rate $L$. The dynamics toward steady state is illustrated in Appendix B. The analysis shows the effect of $L$ and the chemical composition of the percolating water on the weathering reaction, while the remaining parameters (e.g., $[\text{Na}^+]^i$ and $\Sigma_{\text{Si}}^i$) are maintained constant. By setting the time derivatives to zero, the steady state solution can be obtained as

$$ h^* = \left( \frac{L}{K_0} \right)^{\frac{1}{2}}, \quad (29) $$
where the asterisk denotes the steady state. Stability analysis shows that there is a single steady state, which is a stable fixed point for any value of $L$ (Appendix B). Equations (29) and (30) can be solved independently, whereas (31)–(33) are related by the weathering flux $W$ and require equation (22) to be solved. Note that $C_f^*$ depends on the parameters $L$ and $A^I$ and is obtained using the alkalinity constraint. In this section, we study the system (29)–(33) for $\beta = 1$, which corresponds to linear groundwater discharge. We then analyze the system for more realistic cases with $\beta \neq 1$ in section 5.

In the steady state solution (Figure 3), the effects of hydrologic processes are twofold, involving the percolation rate, $L$, and the discharge coefficient, $k_Q$. First, the percolation rate controls the weathering rate through its effect on $C_f$, transported to the weathering zone and the ratio among its components, as assumed in equation (1) and expressed in equation (30). As a consequence, the weathering rate and the weathering products concentrations increase as a function of $L$ (Figure 3). As $L$ increases, more $C_f$ is transported to the weathering zone, which lowers the pH, the ratio $\frac{[\text{alk}]}{[\text{alk}]} = \frac{A^*}{L}$, and the ion activity product $\Theta$. This effect moves the reaction farther from equilibrium. For large values of $L$, the ratio $\frac{A^*}{L}$ tends toward a constant value and, therefore, $\Theta$ and $W$ are no longer affected by further increases in $L$. The second hydrologic control related to the discharge coefficient, $k_Q$, is discussed in more detail in section 4 on water transit times.

A critical implication of the linear approximation for the groundwater dynamics is that in steady state the percolation rate $L$ controls weathering only through the transport of dissolved inorganic carbon (its components) and not through dilution of weathering products in the weathering zone. In fact, for $\beta = 1$, dilution is compensated by an increase in the weathering zone depth, which exposes new mineral surface area to weathering. This results from the fact that the volumetric weathering rate is $h \cdot W$ and that $h$ increases linearly with $L$. For the limiting case $K(L) = 0$ (i.e., $P_{\text{CO}_2} = P_0$ is constant), $W$ and the weathering products are constant with $L$. However, if the mineral surface area is assumed to be nonuniform with depth, the exposed surface area does not increase proportionately to the weathering zone height $h$, and a dilution effect of percolation arises. This represents a fundamental difference between our model and other conceptual models that characterize the role of hydrology on chemical weathering (Berner, 1978; Gabet et al., 2006; Maher & Chamberlain, 2014). In these models, in which the transport of DIC and the increase of exposed mineral surface area with water storage are not accounted for, the hydrologic flux only regulates water residence time and the solute turnover.

For a given value of alkalinity in the percolating water, the weathering rate switches to negative values below a certain value of $L$ (Figure 3). Although this specific condition practically never appears for average field conditions, it is worth discussing the full behavior of the dynamical system as a function of $L$. The point $W = 0$ represents the condition of no net dissolution, marking the limit between undersaturation and oversaturation. In mathematical terms, this happens when the ion activity product is equal to the equilibrium constant

$$\Theta = K_{eq},$$

meaning that the reaction is in detailed balance. For $W = 0$, equations (29)–(33) readily give $A^* = A^I$, $[\text{Na}^+]^* = [\text{Na}^+]^I$, and $\text{Si}_f^* = \text{Si}_f^I$, such that chemical equilibrium is maintained when percolation carries reactants and products of reaction (14) in a ratio equal to the equilibrium constant $K_{eq}$. While $\text{Na}^I$ and $\text{Si}_f^I$ are fixed parameters that do not depend on the percolation rate, the ratio $\frac{A^*}{L}$ decreases with respect to $L$ (Figure 3). In particular, the value of $L$ at which $W$ crosses the axes, $L^*$, corresponds to the value of the ratio $\frac{A^*}{L}$ that satisfies (34). For instance, for given values of $\text{Na}^I$ and $\text{Si}_f^I$, $L^*$ increases approximately linearly with respect to $A^I$ (Figure 4) since lower $\frac{A^*}{L}$ ratios are needed to satisfy (34).
For $L < L^*$, the model predicts oversaturation, that is, $\Theta > K_{eq}$, and precipitation of albite, although this is unlikely under typical field conditions. In the model, oversaturation is reached because $[\text{Na}^+]$ and $S_i$ are kept constant, while the behavior of the model is explored for a wide range of percolation values. When the model is applied to a specific geographic area and experimental data are available, $[\text{Na}^+]$ and $S_i$ can be properly chosen to reproduce the correct field weathering rates.

4. Role of Water Transit Time and Limiting Weathering Regimes

For chemical reactions in which reactants and products are advected by a fluid in and out of the control volume (where the reaction takes place), the fluid transit time, $\tau$, represents a measure of the time available for the system to reach equilibrium. Recall that the transit time is defined as the time that the fluid has spent inside the control volume at the time of exit. Thus, $\tau$ also reflects the degree of dilution caused by the water flowing through. In fact, as flow rates increase, more water with a lower degree of saturation (e.g., $[\text{Na}^+]$ and $S_i$ in percolating water) enters the control volume, causing the solution to dilute. In steady state conditions, transit time can be computed in general as $\frac{V}{\dot{V}}$, where $V$ is the total volume of water inside the control volume.
and $F$ is the flux (e.g., Calabrese & Porporato, 2015). As a result, the water transit time in the weathering zone is given by

$$\tau = \frac{h}{Q} = \frac{h}{k} = \frac{1}{k_Q}. \quad (35)$$

where the last equality is valid when $Q = kh$ (i.e., $\beta = 1$). Therefore, for systems in which the linear approximation holds, the water transit time in the weathering zone is linked to the specific output rate $k_Q$ and does not depend on the percolation rate $L$ or the size $h$ of the weathering zone. Furthermore, this implies that such systems are well mixed, meaning the water exits regardless of its age (i.e., residence time). The transit time $\tau_w$ for the weathering products in solution (time elapsed since their production), $Na^+$ and $Si_T$, can be similarly computed as the ratio of the total mass inside the weathering zone, for example, $h \cdot [Na^+]$, and the output, for example, $Q \cdot [Na^+]$,

$$\tau_w = \frac{h \cdot [Na^+]}{Q \cdot [Na^+]} = \frac{h}{Q} = \tau. \quad (36)$$

Equation (36) shows that the transit time of the weathering products in solution is equal to the transit time of the water. This is to be expected since the weathering zone is assumed to be well mixed.

The effect of water transit time on the weathering rate is demonstrated in the steady state solution (Figure 5). Equations (31)–(33) can be rearranged as

$$A^* = A^i + \tau W^* \left( [H^+]^*, [Na^+]^*, [Si_T]^* \right), \quad (37)$$

$$[Na^+]^* = [Na^+]^i + \tau W^* \left( [H^+]^*, [Na^+]^*, [Si_T]^* \right), \quad (38)$$

$$Si_T^* = Si_T^i + 2\tau W^* \left( [H^+]^*, [Na^+]^*, [Si_T]^* \right). \quad (39)$$

showing that the contribution of mineral dissolution to the alkalinity and weathering products concentrations is modulated by $\tau$ and is independent of $Q$ (and thus $\beta$). The following results in this section are thus not limited to the case of $\beta = 1$, although only when $\beta = 1$ is the transit time equal to the inverse of the specific output rate, $\tau = 1/k_Q$. Equations (37)–(39) show that, for small transit times, dilutive effects prevail, weathering zone concentrations are low and near their values in the percolating water, thus maintaining the system far from equilibrium with high weathering rates. As $\tau$ increases, the weathering zone charges with weathering products, bringing the weathering reaction closer to equilibrium. Following the original approach of Berner (1978), for $\tau \to 0$ the system is in a kinetically limited condition, since the weathering rate is mainly determined by the kinetic parameters, that is, the ion activity product is close to zero, $\Theta \approx 0$, and $W \approx w_{max}$. We refer to the critical transit time below which $W$ approaches $w_{max}$ and becomes independent of $\tau$, as $\tau_\Theta$. On the contrary, transport-limited conditions are reached for large $\tau$, for which $\Theta \approx K_{eq}$ and $W \approx 0$. We therefore identify the critical transit time above which $W \approx 0$ as $\tau_c$. Between these two limiting conditions ($\tau_k < \tau < \tau_c$), the transit time controls the reaction rate through $\Theta$ and we refer to this as the transport-controlled regime. The different weathering regimes can be clearly seen in Figure 6, in which the annual flux $Q_{\text{al}}$ shows two plateaus in the transport and kinetically limited regions. The water transit time can thus be adopted as a parameter to determine boundaries (see section 6) between the transport-controlled and the two limited conditions.

The analysis above was conducted by varying the water transit time $\tau$, while considering a single mineral with given kinetic parameters. Generally, the kinetic parameters could also be varied so that the flux $Q_{\text{al}}$ could be analyzed as function of the Damköhler number (Blattner & Lassey, 1989; Lassey & Blattner, 1988), a dimensionless group given by the product of the water transit time and the kinetic constant expressed in (1/time). Here, however, because we do not vary the kinetic parameters, the system sensitivity to the transit time is equivalent to that of the Damköhler number.
5. Role of Nonlinearity in Groundwater Discharge

In section 3 we analyzed the model in the case of linear groundwater discharge by setting $\beta = 1$. This allowed us to obtain some important physical insights into the role of percolation rate and transit time. With that assumption, in fact, $L$ and $\tau$ have two distinct roles: the former enhances the reaction by transporting reactants, while the latter is an indicator of dilutive effects and is independent of $L$. This assumption not only proves helpful from a theoretical point of view, but it also represents realistically the dynamics of some catchments (e.g., Pearce et al., 1986; Rodhe et al., 1996). In other cases, however, the groundwater does not always behave as a simple linear reservoir and a value of $\beta \neq 1$ may be more representative (e.g., Calabrese & Porporato, 2017; Ceola et al., 2010). We therefore analyze the role of nonlinearity in the groundwater discharge model by studying the system (29)–(33) for different values of $\beta$.

We focus specifically on the solution as a function of $L$, since it was shown in equations (37)–(39) that the steady state solution expressed as a function of $\tau$ is independent of $\beta$ (section 4).

From equation (10) for $\beta \neq 1$, the water table at steady state is not proportional to the percolation rate $L$, that is, $h = (L/kQ)^{1/\beta}$. As a consequence, an increase in the percolation rate is not completely compensated by the exposure of new mineral surface area to weathering (recall the volumetric weathering rate is $h \cdot W$), thus enhancing or weakening the dilution. For $\beta \neq 1$, the limiting case of $K(L) = 0$ does not return weathering rates independent of $L$ (Figure 7d). When $\beta > 1$, dilution prevails over the exposure of new surface area, such that the concentrations of the weathering products decrease and the weathering rates increase (Figure 7). On the contrary, when $\beta < 1$, the exposure of new surface area prevails and the weathering zone concentrates.

By substituting (29) into (35),

$$\tau = \frac{h}{L} = \frac{L^{1/\beta-1}}{kQ^{1-\beta}}.$$  (40)

It is possible to see from (40) that for $\beta \neq 1$, the water transit time $\tau$ is not independent of the percolation rate $L$. For values of $\beta > 1$, as the percolation rate increases, the water transit time decreases, such that both transport of DIC (higher $L$ and $[H_2CO_3^+/HCO_3^-]$) and the increasing dilution (lower $\tau$) enhance the weathering reaction (Figure 7). On the other hand, for values of $\beta < 1$, the transport of DIC (higher $L$ and $[H_2CO_3^+/HCO_3^-]$) is compensated by weaker dilution (higher $\tau$), resulting in lower weathering rates (Figure 7). The difference between weathering rates, $W\ast$, calculated for $\beta \neq 1$ and the ones calculated for $\beta = 1$, which is associated to different degrees of dilution, is shown in Figure 7c. The role of $\beta$ with respect to dilution is particularly emphasized in case of constant $P_{CO_2}$ in the soil pores, $P_{CO_2} = P_0$ (Figure 7d).

6. Interpretation of Field Data

The theoretical framework presented above is now applied to measurements of silicate weathering fluxes for a series of basins with different annual precipitation and runoff values. We consider 14 watersheds with annual precipitation ranging from 500 to 4540 mm/yr and annual runoff from 220 to 3670 mm/yr. This application demonstrates the usefulness of the model to interpret the relationship between climate and long-term Si fluxes. The data we use are reported in Table 1 along with the source papers, in which more details can be found.

The runoff values reported in Table 1 correspond to stream discharge values. These streamflow values typically originate from the contribution of surface runoff and baseflow. While surface runoff has very short timescales (typically less than 1 day) and is produced by the oversaturation of soils, the baseflow represents the slow
component deriving from deep percolation and groundwater dynamics. Besides a portion of percolation that may bypass the weathering zone, the baseflow is the flux of interest in this application. In order to compare the data with our model and in the absence of detailed information, we determined the partitioning of streamflow into surface runoff and baseflow by means of a stochastic soil moisture model (Laio et al., 2001). In particular, we used typical values of frequency of rainfall events, rooting depth, and soil properties, whereas mean rainfall depth and potential evapotranspiration were chosen to match the annual rainfall and streamflow values reported in Table 1. The analysis determined that for all catchments percolation (baseflow) contributes a great fraction of the streamflow, while the potential evapotranspiration reflects the low evapotranspiration expected for the cold climates of the considered areas.

With regard to the weathering fluxes $Q_{Si}$, many factors, such as biological activity, stoichiometry, topography, time variability (e.g., seasonality), and temperature, may affect the weathering reaction. However, the two fundamental parameters that along with climate control the weathering process over long timescales are the transit time and the supply of minerals from the breakdown of the bedrock (Dixon et al., 2016; Hilley et al., 2010; Maher & Chamberlain, 2014; Riebe et al., 2004). We focus on the former and study the weathering fluxes in Table 1 as a function of the percolation rate (climate) and the transit time. The weathering fluxes for the different sites are plotted as a function of $L$ in Figure 8.

In agreement with the data, the model predicts an increase of the Si flux, $Q_{Si}$, with respect to the percolation rate $L$. As $L$ increases, both the Si concentration and the water flux $Q (= L$ at steady state) increase, contributing to higher $Q_{Si}$ values. To identify the mechanisms controlling the weathering rate, we estimated for each watershed the water transit time and compared it to the two critical values, $\tau_k$ and $\tau_t$, introduced in section 4. Recall that when $\tau < \tau_k$, the watershed is kinetically limited whereas for $\tau > \tau_t$, the watershed

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**Figure 6.** Si fluxes as a function of $\tau$ for different values of $L$. Vertical dashed lines indicate the values of critical $\tau$, $\tau_k$, and $\tau_t$. Light gray and light blue areas represent the kinetically limited and transport-limited regions, respectively. Parameters: $[$Na$]^+ = 1$ mol/m$^3$, $Si^0 = 0.02$ mol/m$^3$, $k_Q = \frac{1}{\tau}$ 1/d, $w_{max} = 2.7 \cdot 10^{-6}$ mol/m$^3$/d, and $K_{eq} = 1$ mol/m$^3$.

**Figure 7.** Steady state solutions for (a) [Na$^+$], (b) $Si_T$, and (c) $W$ as a function of the percolation rate $L$ and for given values of $\beta$. The figure shows how the percolation flux also controls dilution when $\beta \neq 1$, while it only transports DIC when $\beta = 1$. (d) Weathering rate as a function of $L$ for constant CO$_2$ pressure in the soil pores, that is, $P_{CO_2} = P_0$. Parameters: $[$Na$]^+ = 1$ mol/m$^3$, $Si_T = 0.01$ mol/m$^3$, $A^2 = 0.2$ eq/m$^2$, $K_{eq} = 10^{-3}$ mol/m$^3$, and $w_{max} = 2.7 \cdot 10^{-6}$ mol/m$^3$/d (chosen according to published data, e.g., White & Brantley, 2003; White et al., 2008).
Table 1
Annual Rainfall, Runoff, Potential Evapotranspiration, Percolation Rate, Silicate Discharge Fluxes, and Estimated Water Transit Times for a Series of Watersheds on Granitic Parent Material

<table>
<thead>
<tr>
<th>Watershed</th>
<th>Rainfall (mm/yr)</th>
<th>Runoff (mm/yr)</th>
<th>Potential ET (mm/day)</th>
<th>Percolation rate (%) of runoff</th>
<th>Silicate flux (mol/km²/yr)</th>
<th>Estimated water transit time (τ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sogndal 1, Norway (Frogner, 1990)</td>
<td>984</td>
<td>875</td>
<td>0.3</td>
<td>814 (93%)</td>
<td>13,000</td>
<td>τ &lt; τ_k</td>
</tr>
<tr>
<td>Sogndal 2, Norway (Frogner, 1990)</td>
<td>959</td>
<td>870</td>
<td>0.24</td>
<td>809 (93%)</td>
<td>16,600</td>
<td>τ ≈ 100</td>
</tr>
<tr>
<td>Emerald Lake, USA (Williams et al., 1993)</td>
<td>1,830</td>
<td>1,410</td>
<td>1.2</td>
<td>1,297 (92%)</td>
<td>39,200</td>
<td>τ ≈ 1,990</td>
</tr>
<tr>
<td>Indian River, USA (Stednick, 1981)</td>
<td>3,300</td>
<td>2,824</td>
<td>1.3</td>
<td>2,541 (90%)</td>
<td>189,600</td>
<td>τ ≈ 18,950</td>
</tr>
<tr>
<td>Exp. Lake, Canada (Allan et al., 1993)</td>
<td>508</td>
<td>225</td>
<td>1</td>
<td>209 (93%)</td>
<td>13,300</td>
<td>τ ≈ 80,600</td>
</tr>
<tr>
<td>Hanley A.B.C., Canada (Feller &amp; Kimmins, 1984)</td>
<td>2,146</td>
<td>1,010</td>
<td>3.3</td>
<td>909 (90%)</td>
<td>98,900</td>
<td>τ &gt; τ_r</td>
</tr>
<tr>
<td>Hanley B.B.C., Canada (Feller &amp; Kimmins, 1984)</td>
<td>2,146</td>
<td>1,240</td>
<td>2.5</td>
<td>1,128 (91%)</td>
<td>93,000</td>
<td>τ &gt; τ_t</td>
</tr>
<tr>
<td>Hanley C.B.C., Canada (Feller &amp; Kimmins, 1984)</td>
<td>2,146</td>
<td>1,040</td>
<td>3.2</td>
<td>936 (90%)</td>
<td>72,800</td>
<td>τ &gt; τ_r</td>
</tr>
<tr>
<td>Jamieson Ck.B.C., Canada (Zeman &amp; Slaymaker, 1978)</td>
<td>4,541</td>
<td>3,668</td>
<td>2.4</td>
<td>3,264 (89%)</td>
<td>153,400</td>
<td>τ ≈ 5,430</td>
</tr>
<tr>
<td>Strengbach, France (Probst et al., 1992)</td>
<td>1,153</td>
<td>1,051</td>
<td>0.29</td>
<td>977 (93%)</td>
<td>60,800</td>
<td>τ ≈ 16,960</td>
</tr>
<tr>
<td>Barhalde, Germany (Stahr et al., 1980)</td>
<td>2,000</td>
<td>1,395</td>
<td>1</td>
<td>1,284 (92%)</td>
<td>120,100</td>
<td>τ &gt; τ_r</td>
</tr>
<tr>
<td>Dargall, UK (Farley &amp; Werritty, 1989)</td>
<td>2,861</td>
<td>2,464</td>
<td>1.1</td>
<td>2,242 (91%)</td>
<td>148,900</td>
<td>τ ≈ 13,210</td>
</tr>
<tr>
<td>Green Burn, UK (Farley &amp; Werritty, 1989)</td>
<td>2,707</td>
<td>2,135</td>
<td>1.7</td>
<td>1,943 (91%)</td>
<td>153,900</td>
<td>τ ≈ 53,880</td>
</tr>
<tr>
<td>White Laggan, UK (Farley &amp; Werritty, 1989)</td>
<td>2,822</td>
<td>2,185</td>
<td>1.7</td>
<td>1,988 (91%)</td>
<td>100,400</td>
<td>τ ≈ 6,690</td>
</tr>
</tbody>
</table>

Note. Parameters used: Root zone depth 30 cm, mean rainfall depth 2 cm, soil parameters for a loamy sand (see Laio et al., 2001). Frequency of rainfall events and potential evapotranspiration (ET) calibrated to match the ET values from White and Blum (1995) (i.e., ET = Rainfall - Runoff).

aData were reported in Table 1 of White and Blum (1995). bData calculated by using a soil moisture dynamics model (Laio et al., 2001).

is transport limited. The intermediate condition, τ_k < τ < τ_t, defines instead transport-controlled watersheds. Based on the parameters adopted in Figure 8, we estimate τ_k ≈ 100 days and τ_t ≈ 10^6 days. The estimated τ values and their comparison with τ_k and τ_t are reported in Table 1. In particular, while most of the watersheds are transport controlled, Sogndal 1 in Norway is kinetically limited, while Hanley in Canada and Barhalde in Germany are transport limited.

Note that the estimates of transit time do not depend on the functional form used for Q. As shown in section 4, the τ values are in fact computed, for given percolation rate and Si flux, by solving equations (37)–(39), for which at steady state Q(h) is not needed. On the other hand, since the actual mineralogy of the basins is not known exactly, kinetic and equilibrium constants (which were chosen for the single mineral albite) as well as the stoichiometry of the reaction represent a source of uncertainty. Overall, Figure 8 suggests that the model presented here is suitable for interpreting the role of hydrologic factors such as the percolation rate and the water transit time on the weathering fluxes. This framework requires only parameters of clear interpretation...
that are becoming readily available in the literature and are amenable to large-scale analysis under different geologic and climatic contexts. Lastly, we stress that the tools developed here allow predictions over long timescales, so that the interplay between chemical weathering, soil acidification, clay formation processes, and carbon cycle can be explored.

7. Conclusions

We developed a nonlinear dynamical system with five state variables and one algebraic constraint to describe the main features of mineral dissolution in the weathering zone. The model links the percolation rate to the input of dissolved inorganic carbon to the weathering zone through production of CO$_2$ in the near surface root zone, its speciation, and transport to the subsurface weathering sites. The system was analyzed under constant hydrologic forcing, representing an average percolation rate, to investigate the role of deep hydrologic fluxes and the associated water transit time on the weathering rate and approach to steady state.

The model was first studied by assuming that the groundwater is a linear system. Under this assumption, the role of hydrological processes on chemical weathering rates is twofold. First, the percolation rate itself controls the weathering rate only by stimulating CO$_2$ production in the root zone and transporting the dissolved inorganic carbon components to the subsurface weathering zone. As the percolation rate increases, more DIC with higher $[\text{H}_2\text{CO}_3^{\ast}] / [\text{HCO}_3^{-}]$ ratio is transported to the weathering zone, so that $\Theta$ decreases and the reaction accelerates. Second, the dilutive effects commonly associated with the percolation rate were found to be regulated by the water transit time alone (i.e., the weathering zone discharge coefficient). When the hypothesis of linear system is relaxed, the transit time is dependent on the percolation rate, such that the latter also regulates dilutive effects.

The water transit time $\tau$ expresses the extent of dilutive effects and the turnover of the weathering products. For small transit times, the weathering zone is constantly diluted so that far from equilibrium conditions are maintained, that is, high weathering rates, while for large $\tau$ the system approaches near-equilibrium conditions, that is, low weathering rates. The model was then applied to a set of watersheds for which we estimated the water transit times and identified the limiting mechanisms to demonstrate its ability to identify limiting mechanisms of chemical weathering from climate and water chemistry data.

This work can be extended by considering interannual, seasonal, and storm event-scale variability in the percolation flux. Introducing temporal variability would provide a framework to investigate the role of time-varying climatic conditions as well as predict long-term weathering fluxes by means of upscaling techniques. Furthermore, the model could be coupled to soil moisture and $P_{\text{CO}_2}$ dynamics in the root zone, such that the role of surface ecohydrological processes as an interface between the atmosphere and the critical zone that propagates high-frequency hydroclimatic fluctuations could be explored.

Appendix A: Overall Weathering Rate

We determine the weathering rate for the overall weathering reaction of albite to kaolinite, equation (14). Assuming that the dissolution of albite is the limiting reaction (e.g., Li et al., 2014; White, 1995), $k_{\text{alb}} \ll k_{\text{kaol}}$, the rate of the overall reaction can be approximated by the rate of dissolution of albite $W \approx W_{\text{alb}}$, while the precipitation of kaolinite can be considered to approach equilibrium relatively fast. Thus, the weathering rate for the overall reaction reads

$$W \approx W_{\text{alb}} = k_{\text{alb}} \left[1 - \frac{1}{K_{\text{eq,alb}} \left[\text{Al}^{3+} \right] \left[\text{Na}^{+} \right] \left[\text{HCO}_3^{-}\right]^{4} \left[\text{H}_4\text{SiO}_4\right]^{3}}{\left[\text{H}_2\text{CO}_3\right]^{4}}\right]. \tag{A1}$$

Since precipitation of kaolinite is considered an equilibrium reaction, from the law of mass action one obtains

$$\frac{[\text{H}_2\text{CO}_3]^{3}}{[\text{Al}^{3+}] [\text{HCO}_3^{-}]^{3}} = K_{\text{eq,kaol}} \left[\text{H}_4\text{SiO}_4\right]. \tag{A2}$$

which substituted into (A1) gives

$$W = k_{\text{alb}} \left[1 - \frac{1}{K_{\text{eq,alb}} K_{\text{eq,kaol}} \left[\text{Na}^{+} \right] \left[\text{HCO}_3^{-}\right] \left[\text{H}_4\text{SiO}_4\right]^{2}}{\left[\text{H}_2\text{CO}_3\right]^{4}}\right]. \tag{A3}$$
Expression (A3) can now be rearranged by introducing $K_{eq,alb}K_{eq,kao} = K_{eq}$.

$$W = k_{alb}\left[1 - \frac{1}{K_{eq}}\left[\frac{[\text{Na}^+][\text{HCO}_3^-][\text{H}_4\text{SiO}_4]^2}{[\text{H}_2\text{CO}_3]}\right]\right] = k_{alb}\left[1 - \frac{\Theta}{K_{eq}}\right].$$ \hspace{1cm} (A4)

**Appendix B: Approach to Steady State**

Percolation rate and water transit time affect the temporal evolution of the system toward steady state. In this Appendix, we compute numerically the trajectories for the system with different initial conditions.

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**Figure B1.** (left column) Time evolution for $[\text{Na}^+]$, $\text{Si}_T$, and $W$ for different values of $L$. Black solid lines computed for $L=L^*$ (chemical equilibrium at steady state), red solid lines for $L=0.01$ m/d (dissolution), and blue solid lines for $L=0.001$ m/d (precipitation). Initial conditions (bottom row) $h=0$ m, $C_T=0$ mol/m$^3$, $A=0$ eq/m$^3$, $[\text{Na}^+] = 0$ mol/m$^3$, $\text{Si}_T=0$ mol/m$^3$ and (top row) $h=0$ m, $C_T=0$ mol/m$^3$, $A=0$ eq/m$^3$, $[\text{Na}^+] = 2$ mol/m$^3$, $\text{Si}_T=0.02$ mol/m$^3$. (right column) Time evolution for $[\text{Na}^+]$, $\text{Si}_T$, and $W$ for different values of $\tau$ and fixed percolation rate, $L=0.005$ m/d (dissolution). Blue lines calculated for $\tau=1$ day and red lines for $\tau=10^4$ days. Initial conditions $h=0$ m, $C_T=0$ mol/m$^3$, $A=0$, $[\text{Na}^+] = 0$ mol/m$^3$, $\text{Si}_T=0$ mol/m$^3$ (bottom row) and $h=0$ m, $C_T=0$ mol/m$^3$, $A=0$ eq/m$^3$, $[\text{Na}^+] = 2$ mol/m$^3$, $\text{Si}_T=0.02$ mol/m$^3$ (top row). Trajectories in Figure B1 (left column) are calculated for $k_Q=10^{-3}$ 1/day, $A^l = 0.2$ eq/m$^3$, while the remaining parameters are the same as in Figure 3.
Recall that oversaturation is predicted in the model due to the assumption of constant concentrations of Na\(^+\) and Si\(_T\) in the percolating water; however, this condition is rarely seen in saprolite environments since [Na\(^+\)] and Si\(_T\) may be functions of \(L\). Therefore, the following analysis is meant to be only descriptive of the dynamical system introduced in this model.

Figure B1 shows temporal evolutions of the weathering products, [Na\(^+\)] and Si\(_T\), and the weathering rate \(W\) for different values of the percolation rate \(L\), on the left column, and transit time \(\tau\), on the right column. Depending on initial conditions and the chosen value of \(L\), the system may dissolve, precipitate, or switch between the two regimes as it approaches steady state. In Figure B1 (left column), the solid black line corresponds to the trajectory that at steady state guarantees chemical equilibrium (\(W = 0\)). Below this black line, the trajectories correspond to steady states in which the mineral precipitates, \(W < 0\). However, depending on the initial condition, solutes may initially dissolve, that is, \(W > 0\). As \(L\) increases, the trajectories stay above the black line and the system at steady state is dissolving the mineral. Again, the initial condition might be such that precipitation initially occurs.

The trajectories in Figure B1 are calculated with values of [Na\(^+\)] and Si\(_T\) that differ by 2 orders of magnitude, [Na\(^+\)] \(\gg\) Si\(_T\). These values were chosen to elucidate the role of \(W\) on the temporal dynamics by comparing the dynamics of [Na\(^+\)], which is driven mainly by the input in the percolation, to that of Si\(_T\), for which \(W\) is a relevant driving term. The value of [Na\(^+\)] was chosen such that \(\frac{1}{2}[\text{Na}^+] \gg W\), and therefore, the dynamics of [Na\(^+\)] is mostly driven by the constant input [Na\(^+\)]\(^2\). This results in smooth transitions toward the steady state. Furthermore, as can be noted from (32), for [Na\(^+\)] \(\gg\) W the steady state values do not diverge considerably from [Na\(^+\)]\(^2\) (i.e., [Na\(^+\)] \(\approx\) [Na\(^+\)]\(^2\)) and do not show sensitivity to \(L\). On the contrary, the input of Si\(_T\) from percolation is of the same order as the production from the reaction, \(\frac{1}{2}\text{Si}_T \approx W\), so that the dynamics of Si\(_T\) is driven by both Si\(_T\) and \(W\). As can be seen in equation (33), the steady state value of Si\(_T\) is dictated by the interplay of Si\(_T\) and \(W\) and, as a result, is dependent on the percolation rate \(L\). While the trajectories for Si\(_T\) are smooth, they overshoot the steady state when the weathering reaction switches sign. The overshooting is illustrated in Figure B2 where a projection of the phase space into the [Na\(^+\)], Si\(_T\) plane is plotted. As an example, the blue trajectory in Figure B2a, calculated for an initial condition Si\(_T\) = 0 (Figure B1), is first attracted toward the center of the graph by Si\(_T\), and the initial dissolution, but then, as the solutes start to precipitate, the trajectory reverses direction and goes backward to the steady state value indicated by the blue star.

The transit time is strictly related to the typical timescale of the system, as shown in Figure B1 (right column). Unlike the percolation rate \(L\), changes in transit time \(\tau\) do not cause the system to switch between precipitation and dissolution. Because of the fast removal of the products by the water flow, the reaction proceeds at high rates in case of low \(\tau\) values and the system needs less time to reach its steady state. As the transit time increases, however, the system is closer to equilibrium throughout its trajectory to steady state, resulting in lower rates and longer times to reach steady state. As mentioned in the previous section, \(\tau\) is an important parameter for the weathering reaction. Recall that short transit times indicate kinetic limitation,

**Figure B2.** Phase space dynamics projection into the [Na\(^+\)], Si\(_T\) plane. The stars indicate the steady states. (a) Blue and red trajectories correspond to the blue and red trajectories in Figure B1 (left column). (b) Blue and red trajectories correspond to the blue and red trajectories in Figure B1 (right column).
whereas large values of $\tau$ indicate transport limitation. Therefore, this dynamics suggests that systems that tend to be kinetically limited react fast to external perturbation and relax to their steady state much faster than transport-limited systems.

Acknowledgments
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References


In the originally published version of this article, there were two minor errors, neither of which affected the conclusions of the manuscript. The following changes have been made:

1. Equation 13 was missing a double arrow. The correct equation is: $\text{Equation 13}$.
2. Figure 3 was missing a label. The correct figure label is: \text{Figure 3}.

These corrections do not affect the overall conclusions of the article.