

Reservoir theory for studying the geochemical evolution of soils

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[1] Linking mineral weathering rates measured in the laboratory to those measured at the landscape scale is problematic. In laboratory studies, collections of minerals are exposed to the same weathering environment over a fixed amount of time. In natural soils, minerals enter, are mixed within, and leave the soil via erosion and dissolution/leaching over the course of soil formation. The key to correctly comparing mineral weathering studies from laboratory experiments and field soils is to consistently define time. To do so, we have used reservoir theory. Residence time of a mineral, as defined by reservoir theory, describes the time length between the moment that a mineral enters (via soil production) and leaves (via erosion and dissolution/leaching) the soil. Age of a mineral in a soil describes how long the mineral has been present in the soil. Turnover time describes the time needed to deplete a species of minerals in the soil by sediment efflux from the soil. These measures of time are found to be sensitive to not only sediment flux, which controls the mineral fluxes in and out of a soil, but also internal soil mixing that controls the probability that a mineral survives erosion. When these measures of time are combined with published data suggesting that a mineral's dissolution reaction rate decreases during the course of weathering, we find that internal soil mixing, by partially controlling the age distribution of minerals within a soil, might significantly alter the soil's mass loss rate via chemical weathering.

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1. Introduction

[2] The burgeoning field of critical zone research has renewed scientific interest in placing soils within the wider Earth surface and ecological contexts [Brantley *et al.*, 2007; Anderson *et al.*, 2008]. In the geomorphology community, the word soil generally refers to material that is physically disturbed and is moving downslope. This material is converted from chemically weathered but physically inactive parent material (often called saprolite) [e.g., Dietrich *et al.*, 1995; Heimsath *et al.*, 1997; Riebe *et al.*, 2003; Mudd and Furbish, 2004]. Geomorphic sculpting of soil mantled landscapes is largely driven by the processes occurring within or at the boundaries of this physically disturbed zone. In parallel, the biogeochemistry community has focused on the soil carbon cycle and weathering in the context of atmospheric CO₂ [Amundson, 2004; Hren *et al.*, 2007; Ferrier and Kirchner, 2008; Gabet and Mudd, 2009] and terrestrial ecosystem processes [e.g., Porder and Chadwick, 2009]. Recently, researchers have increasingly sought to link biogeochemical cycles to the geomorphic evolution of land-

scapes [Blum *et al.*, 2002; Porder *et al.*, 2006; Yoo *et al.*, 2007, 2009]. Biogeochemists often consider soil to be the entire weathering profile from the boundary between chemically unaltered parent material and chemically altered material to the surface, but it has been demonstrated that weathering rates in the thinner but more porous and physically disturbed layer are at least as great as in the portion of the weathering zone that lacks physical disturbance [Anderson *et al.*, 2002]. Considering landscapes evolve geomorphically over thousands to millions of years [Fernandes and Dietrich, 1997; Roering *et al.*, 2001; Baldwin *et al.*, 2003; Mudd and Furbish, 2007], it is critical to quantify rates of biogeochemical change over these timescales.

[3] The weathering zone can be largely divided into two sublayers: a physically disturbed zone (PDZ) wherein soil is disturbed by biophysical processes and a physically undisturbed but chemically altered zone (CAZ) [see Yoo and Mudd, 2008b]. There is a great uncertainty in delineating the vertical reach of biophysical and chemical processes in soils, and researchers have begun to study how chemical weathering in the CAZ responds to tectonics and climate [e.g., Dixon *et al.*, 2009]. In the geomorphology community, the PDZ is referred to as "soil" [e.g., Dietrich *et al.*, 1995; Heimsath *et al.*, 1997; Roering *et al.*, 2001] or "regolith" [e.g., Small *et al.*, 1999; Anderson, 2002]. Soil scientists, however, extend the definition of soil into weathered but physically undisturbed material (i.e., the C horizon). The PDZ is equivalent to the biomantle [Johnson, 1990] in soils

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predominantly perturbed via bioturbation [e.g., *Gabet et al.*, 2003].

[4] If the soil surface is level, lateral movements of the layer's minerals and organic matter are randomly directed, and there is no net lateral sediment transport [*Yoo and Mudd*, 2008b]. On sloping terrain, however, the perturbed materials are more likely to move downslope because of the presence of gravity [*Roering*, 2004; *Furbish et al.*, 2009]. Consequently, a net mass flux occurs in the downslope direction, and soil on sloping terrain loses or gains mass depending on the net mass exchange with the neighboring soils upslope and downslope: this drives sediment transport. On sloping landscapes, therefore, the PDZ is synonymous with the colluvial zone. At the bottom of the physically mobile layer, mass flux occurs from the in situ layer underlying the PDZ, and this flux has been termed soil or regolith production [e.g., *Heimsath et al.*, 1997].

[5] In this contribution we focus on the geomorphically active portion of the weathering zone, i.e., the PDZ. We do note that volumetric collapse associated with the mass loss via chemical weathering does occur [*Chadwick et al.*, 1990], so the CAZ can occasionally play a role in the morphologic evolution of landscapes. Regardless of whether one considers both the PDZ and CAZ or the PDZ alone, however, quantifying rates of processes in the weathering zone inevitably requires two variables: the degree to which physical and chemical properties of the weathering zone change and the length of time over which the processes that induced the changes have been active.

[6] The nature and rate of weathering reactions can change depending on the time minerals spend in the weathering zone [*Brantley*, 2008; *Yoo and Mudd*, 2008a], yet there is no consistent framework for measuring time from the laboratory to eroding and noneroding landscapes. This is surprising considering time is one of the soil forming factors [*Jenny*, 1941]. In the conceptual framework by *Jenny* [1941], the term soil "formation" implicitly defines time as a unidirectional parameter upon which soil properties depend. The unidirectional nature of time makes it unique among the five soil-forming factors. The other soil-forming factors, climate, parent material, biota, and topography, encompass a variety of physical parameters. For example, climate is described using temperature, rainfall, and their temporal and spatial distribution. Parent material is represented based on the rock types, mineralogical, and elemental compositions. Likewise, biota indicates potential gene pools in terms of the diversity of biological species or their carbon and nitrogen cycling characteristics, etc. Lastly, one can attempt to capture the configuration of topography using attributes such as elevation, slope gradient, and curvature. Time is unique, however, because it has only one unit of measurement, but it can, for any given soil, have a number of different values based on the frame of reference.

[7] Quantification of time requires careful consideration of the reference point upon which the "clock" is activated. Time, as a factor of soil formation, has been defined as the "elapsed time since deposition of material, the exposure of the material at the surface, or formation of the slope to which the soil relates [*Birkeland*, 1999]." This definition is equivalent to considering the time zero in soil formation as the moment that geomorphic surfaces are stabilized due to the cessation of erosion or deposition. The length of time

since stabilization is defined as the soil age. Numerous studies of soil chronosequences (a series of soils that share similar climate, parent material, topography, and organisms but have varying ages) have used this definition of soil age as a substitute for time. Such studies not only demonstrated that various soil properties evolve over time but also provided rare opportunities to estimate long-term rates of biogeochemical processes in soils. In chronosequences, rates of processes can be established where relatively clear causal relationships between processes and changes in soil properties are evident. Because soil formation occurs over timescales much greater than a human lifespan, soil chronosequences have been an important source of knowledge regarding the rates and trajectory of soil property changes and pedogenic processes.

[8] The concept of soil age, by definition, requires landforms on which geomorphic processes of erosion and deposition no longer destabilize the surface. Thus, the concept of soil age, while tremendously powerful within the context of the soil chronosequence, has limitations, particularly in eroding landscapes [*Almond et al.*, 2007; *Yoo et al.*, 2007, 2009; *Yoo and Mudd*, 2008b]. Eroding landscapes, however, constitute the vast majority of the land surface. Indeed, even on noneroding surfaces, it has recently been demonstrated that the concept of soil age needs to be expanded in order to apply short-term laboratory measurements to the long-term geochemical evolution of soils [*Yoo and Mudd*, 2008a]. Soils in eroding or depositional landscapes have been neglected relative to the soils in low relief landscapes that are agriculturally important and do not feature the added complexity of lateral sediment transport. Population growth, however, makes it likely that future agricultural expansion will occur in sloping, rather than flat, landscapes [*Brown*, 1981]. Additionally, the chronosequence approach is limited because of the relative paucity of well-characterized soils that share similar environments but span a range of ages.

[9] A topographic sequence of soils that are connected via material fluxes such as erosion and deposition and subsurface water flow has been termed a soil catena (from the Latin for "chain") [*Birkeland*, 1999]. To counter the problem that defining soil age is problematic on catenae undergoing erosion and deposition, two distinct conceptual models have been proposed. *Butler* [1959] proposed that soil formation on hillslopes was periodic in nature, with portions of hillslopes being temporarily unstable. These unstable portions of hillslopes experience erosion or deposition, followed by a period of stability and soil formation, resulting in stratigraphic records of buried soils in depositional slopes [*Birkeland*, 1999]. Thus, dynamic landscapes are composed of a mosaic of soils of different "ages" defined as the time since local stabilization [*Butler*, 1959]. This concept of periodic soil formation is called the K cycle. In terrain that experiences intermittent slumping and landsliding, this concept may be applicable [e.g., *Walker*, 1962], but in most soil, mantled landscapes soil formation is thought to occur continuously or in frequent, small events [e.g., *Carson and Kirkby*, 1972; *Birkeland*, 1999; *Dietrich et al.*, 2003]. In summary, geomorphic processes of erosion and deposition have been viewed in competition with soil formation [*Birkeland*, 1999]. In such landscapes, soil production, i.e., the generation of new soil from underlying

parent material, replenishes materials lost to erosion and sediment transport. Thus, *Nikiforoff* [1942] reasoned that soils may approach a dynamic equilibrium in which ongoing renewal of soil materials is balanced by the geochemical alteration of these materials. More recently, *Johnson and Watsonstegner* [1987] presented a concept of dynamic denudation, where both chemical weathering and sediment transport is balanced by soil formation.

[10] Laboratory experiments of chemical weathering subject a collection of minerals to the same weathering history, but the inorganic fraction of natural soils is a body of minerals with disparate weathering histories. The soil age does not consider the distribution of times that mineral grains have been exposed to weathering environments. What is needed is an approach in which geochemical reactions of minerals as quantified in a laboratory can be applied to understanding weathering histories of soils. *Yoo and Mudd* [2008a] examined this issue by simulating the evolution of a soil's mineral composition during its initial 100 ka of formation on noneroding terrain. They demonstrated that the time minerals stay within the soil and thus experience the soil's weathering environment is much shorter than the soil age. They also demonstrated that both specific dissolution rates and sizes of minerals dramatically affect their longevity within soils. Finally, they found that total soil weathering rates are underestimated by orders of magnitude when laboratory-based weathering rates are applied to a soil age rather than the distribution of mineral ages within the soil. The discrepancy of mineral chemical weathering rates from the two scales has been highlighted as one of the major challenges in weathering science [*Brantley et al.*, 2007].

[11] Whereas soil age has been applied to noneroding soils, studies of eroding landscapes have focused on the turnover time [*Small et al.*, 1999; *Anderson et al.*, 2002; *Amundson*, 2004; *Mudd and Furbish*, 2006; *Almond et al.*, 2007]. In an eroding landscape the turnover time is generally defined as the thickness of the PDZ (usually referred to as soil in geomorphic papers) divided by the erosion rate and assumes a balance between erosion and the entrainment of material into the PDZ. Prior studies of soils have commonly referred to the turnover time as the residence time, but here we adopt the naming conventions of reservoir theory (see section 2). While the turnover time is a more appropriate measure of time in an eroding landscape than the concept of soil age, it too has drawbacks. The turnover time does not account for the distribution of times that minerals spend in the weathering zone. *Mudd and Furbish* [2006] quantified the distribution of times minerals spend in the PDZ, but they did not link the distribution of particle ages with chemical weathering rates. *Yoo and Mudd* [2008a] demonstrated, however, that understanding the distribution of mineral ages is crucial to understanding weathering fluxes from a soil of different ages.

[12] Here we extend the work of *Yoo and Mudd* [2008a] to eroding landscapes and also formally define a series of measures of time that can be used to assimilate laboratory-scale experiments into landscape-scale weathering environments. At the heart of this approach is the explicit treatment of soil (as defined in the geomorphic sense) as a collection of individual minerals and organic debris that are being continuously replaced by new materials due to sediment

transport, soil production, and net primary productivity. This perspective, when combined with the need to define time in the context of weathering and sediment transport that accounts for mineral weathering histories and the rate of biogeochemical alteration, leads us to the specific objective of this paper: the modification of reservoir theory for studying geochemical evolution of soils.

2. Background: Measures of Time in Reservoir Theory

[13] Reservoir theory describes the change in abundance of a substance in a reservoir in terms of its inputs and outputs through the reservoir. This reservoir can be defined as any volume enclosed by a boundary such as a lake, an ecosystem, or in this case a soil or subcomponents of a soil. *Eriksson* [1971] was the first to present a mathematical description of reservoir theory to Earth and ecological scientists. In this paper, given the common confusion and inconsistency of the terms, we strictly follow the definitions and nomenclature stated in *Rodhe* [2000]. While reservoir theory has been applied to the cycling of soil carbon [*Trumbore*, 1993], the theory has not been used to understand the biogeochemical evolution of soils. Below we argue that reservoir theory can be used to link mineral scale chemical weathering to landscape scale solute fluxes. We begin with a basic overview of the measures of time in reservoir theory.

2.1. Age

[14] For any given particle in a reservoir, there is a time spanning the moment that particle entered the reservoir to the moment the reservoir is measured. This time is the particle age. Just as an age can be given to an individual particle, a mean age can be given to a collection of particles in a reservoir. A notation $\psi(\tau)$, with the unit of frequency (T^{-1}), is used to represent the probability density function of particle ages.

$$\psi(\tau) = \frac{1}{M_{\text{tot}}} \frac{dM_{\tau}}{d\tau}, \quad (1)$$

where M_{tot} is the total mass of the particles of interest in the reservoir and M_{τ} is the mass of particles with ages less than or equal to τ . Because $\psi(\tau)$ is a probability density function, it must satisfy the condition:

$$\int_0^{\infty} \psi(\tau) d\tau = 1. \quad (2)$$

The mean age of the particles in the reservoir, $\langle \tau_a \rangle$, can be calculated from the age density function as:

$$\langle \tau_a \rangle = \int_0^{\infty} \tau \psi(\tau) d\tau. \quad (3)$$

2.2. Residence Time

[15] Whereas age is determined for particles within the reservoir, residence time is defined for particles leaving the reservoir. The times that a particle enters and leaves the reservoir can be determined. The difference between the two

times is the length that the particle resides in the reservoir. This time is called the residence time or transit time τ_r . The notation $\phi(\tau)$, with the unit of frequency (T^{-1}), is used to represent the probability density function of particles' residence times. Particles can leave the reservoir, and the mass flux (e.g., the rate that mass is lost per unit area) of all particles of a given type is defined as Q_{tot} . Particles that leave the reservoir have resided in the reservoir for a certain amount of time, so we can define a partial mass flux Q of particles that resided within the reservoir longer than the period of τ . The difference between these two fluxes is equal to the rate that the mass of the particles younger than τ changes within the reservoir [e.g., Eriksson, 1971; Rodhe, 2000]:

$$Q_{\text{tot}} - Q(\tau) = \frac{dM_\tau}{d\tau}. \quad (4)$$

The residence time distribution is related to the flux through

$$\phi(\tau) = \frac{1}{Q_{\text{tot}}} \frac{dQ(\tau)}{d\tau}. \quad (5)$$

By inserting equation (1) into equation (4) and incorporating the result into equation (5), we find that

$$\phi(\tau) = -\frac{M_{\text{tot}}}{Q_{\text{tot}}} \frac{d\psi(\tau)}{d\tau}. \quad (6)$$

Like the probability density function of age, the probability density function of residence time must satisfy the condition

$$\int_0^\infty \phi(\tau) d\tau = 1. \quad (7)$$

The mean residence time or mean transit time for the particles $\langle\tau_r\rangle$ is

$$\langle\tau_r\rangle = \int_0^\infty \tau\phi(\tau) d\tau. \quad (8)$$

2.3. Turnover Time

[16] Turnover time τ_0 is the length of time that a kind of particle is completely depleted by the outgoing flux of the substance. It is calculated by dividing the total mass of the particles within the reservoir (M_{tot}) by the outgoing mass flux of that kind of particle (Q_{tot}). Unlike the residence time and age, the turnover time is a value for the collective entity of the particles of interest and is not defined for individual particles.

$$\tau_0 = \frac{M_{\text{tot}}}{Q_{\text{tot}}}. \quad (9)$$

When the reservoir is in steady state for a kind of particle, the abundance of these particles within the reservoir does not change with time. The flux leaving the reservoir is equal to the flux entering the reservoir. In such a steady state condition, the turnover time is equal to the mean residence time of the particles.

2.4. Soil Age Versus Reservoir Theory

[17] Soil age is distinct from the three measures of time as defined in reservoir theory. Whereas measures of time in

reservoir theory concern a specific substance that fills the reservoir, soil age represents the length of time since the soil as a reservoir was created. The definition of soil age does not include the physical dynamics of the soil constituents, whereas the measures of time in reservoir theory do. It applies to both the PDZ and the CAZ (although here we focus on the PDZ).

3. Reservoir Theory Applied to Distinctive Soil Systems

[18] Reservoir theory is designed for open systems that exchange materials with the surrounding environment. In this regard, the PDZ is ideally suited to be examined using reservoir theory. We examine four distinct models of the PDZ (Figure 1). In the following simulations, the PDZ is considered as a box where mineral grains enter from the underlying parent material and leave via physical erosion or chemical weathering. After a length of time τ since the entrainment of minerals into the PDZ, the fraction of mineral mass that remains in the soil depends on the mass loss via chemical weathering within the soil. These reactions are functions of temperature, solute chemistry, and other factors, which may include time. Indeed, *White and Brantley* [2003] compiling data from their own laboratory experiments as well as a large number of field studies found that weathering rates for several rock forming minerals were strongly dependent on how long these minerals had been in the weathering zone because of the depletion of weathering-susceptible sites on the mineral surface as well as the occlusion of this weatherable surface by secondary minerals. *Gabet and Mudd* [2009] combined the relationships between rate coefficients and surface roughness in the study by *White and Brantley* [2003] into a single statement describing the fraction of a primary mineral remaining after chemical weathering for a duration of τ :

$$F_\tau = \exp\left(\frac{k\tau^{1+\sigma}}{1+\sigma}\right), \quad (10)$$

where k and σ are empirical coefficients constrained by field and laboratory data in the study by *White and Brantley* [2003] and are specific to mineral species' weathering susceptibility. For conservative minerals, for example, $k = 0$. In our analyses, we focus on the following minerals that reflect a wide range of susceptibility to dissolution reactions: quartz, K feldspar, plagioclase, and biotite. The data from *White and Brantley* [2003] are used in equation (10) to calculate the dissolution rate of K feldspar, plagioclase, and biotite; parameter values are shown in Table 1. Quartz is assumed to be conservative (i.e., it does not lose mass to chemical weathering) because its rate of dissolution is several orders of magnitude slower than the other minerals we model here. It should be emphasized that for the minerals that are susceptible to dissolution and leaching, the total outgoing flux of the minerals leaving a soil (i.e., Q_{total} in equations 4–6) is composed of both solid mass removed by physical processes and mass loss via chemical weathering.

3.1. Noneroding Landscapes

[19] Here we focus on parts of the landscape that have neither deposition nor erosion at their surface and are not

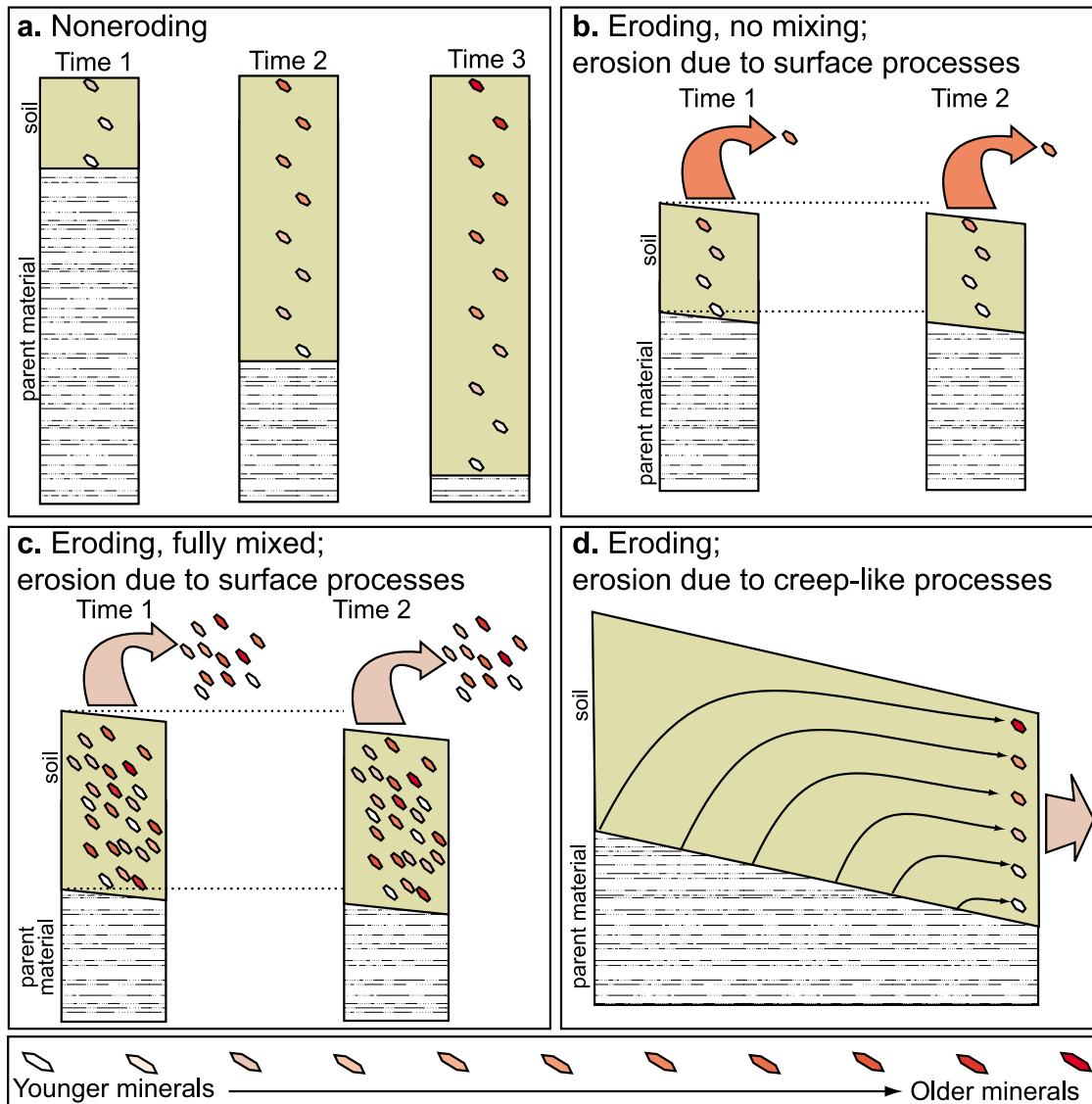


Figure 1. Schematic drawing of the four distinct soil models; we apply reservoir theory to each of these models.

being transported laterally, e.g., the surface of a fluvial terrace. Such locations are commonly used in soil chronosequence studies. The soil age T_s may be defined as the time elapsed since the stabilization of the geomorphic surface upon which the weathering zone develops. As time passes, weathering and disturbance fronts move down through the parent material, and previously pristine minerals are entrained into the weathering zone. Each mineral grain in the weathering zone therefore has its own age that is counted from the moment that the mineral entered the soil due to the downward propagation of the weathering front. The age of each mineral grain increases as the mineral survives dissolution in the weathering zone. Thus, we can consider minerals of the same species that entered the weathering zone when the soil age was t that can range from zero to the current soil age T_s , and where $t = 0$ is the time when the geomorphic surface was stabilized. The age of a mineral at time T_s is τ and is equal to the soil age minus the

time the mineral entered the weathering zone (i.e., $\tau = T_s - t$). The mass of minerals with ages less than τ can be obtained by integrating the rate that the mass of the minerals entered at t ($\rho_t P_t$; where ρ_t is the bulk density of underlying parent material and P_t is the soil production rate in dimensions of

Table 1. Parameter Values for Several Minerals^a

Parameter	K-feldspar	Plagioclase	Biotite
σ (unitless)	-0.447	-0.364	-0.403
kD ($m\ y^{-1}$)	0.891×10^{-7}	0.902×10^{-7}	1.780×10^{-7}
D (mm)	0.1	0.1	0.1

^aOriginal data from *White and Brantley* [2003], as recalculated by *Gabet and Mudd* [2009]. Potassium feldspar is assumed to be of orthoclase composition, and plagioclase is assumed to be of albite composition. The parameter k is a function of the particle diameter D , whereas the quantity kD is only a function of the empirical coefficients determined by *White and Brantley* [2003].

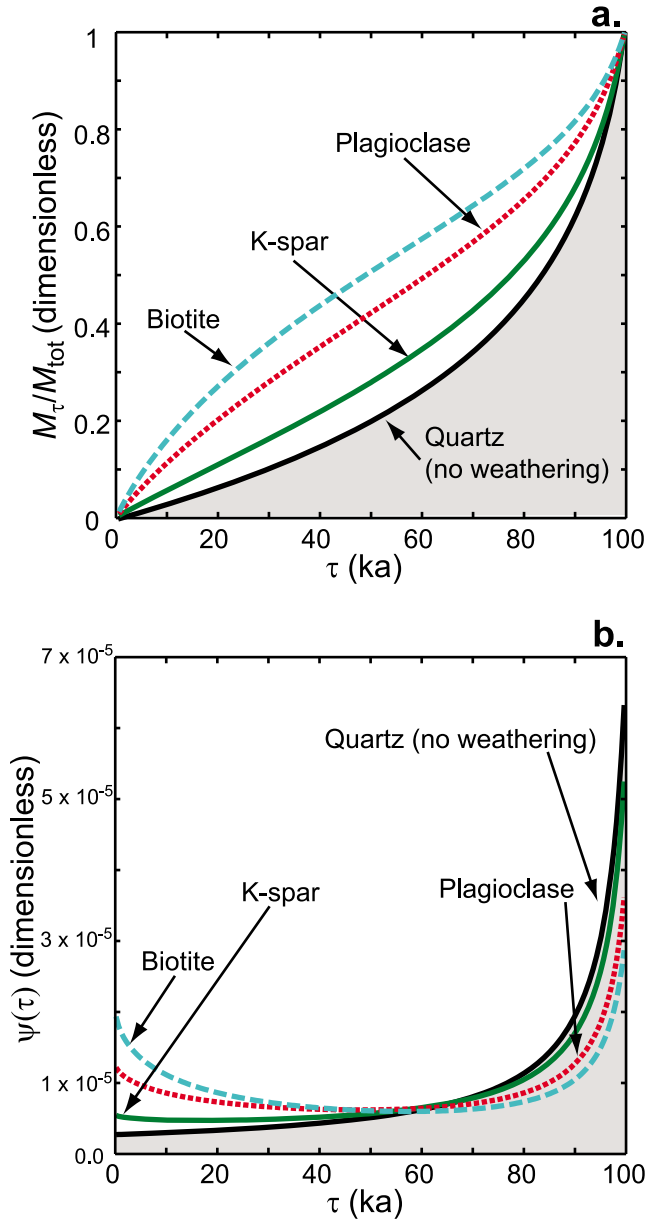


Figure 2. Fraction of mineral mass with (a) age less than τ (i.e., M_τ) and (b) mineral age density function of a noneroding soil. Note that M_τ/M_{tot} is the cumulative density function of mineral age. Soil production parameters are listed on the plot. Soil age = 100 ka, $W_0 = 0.1$ mm/yr, $\rho_s = 1600$ kg/m³, $\rho_r = 2000$ kg/m³, and $\gamma = 0.5$ m. Mineral properties shown in Table 1 (grains have a starting diameter of 0.1 mm).

length per time) times the fraction of the mass surviving the loss via chemical weathering F_{T_s-t} over the time length of τ ,

$$M_\tau = \int_{T_s-\tau}^{T_s} \rho_r P_t F_{T_s-t} dt. \quad (11)$$

In equation (11), both P and F are functions of time. Upon integration, P is evaluated at time t and F is evaluated at time $T_s - t$ (see equation 15). It has been found that the rate at which material is physically entrained into the PDZ, i.e.,

the rate of soil production, is a function of the thickness of the PDZ [e.g., *Heimsath et al.*, 1997]:

$$\rho_r P_t = \rho_s \frac{\partial h_t}{\partial t} = \rho_r W_0 \exp\left(-\frac{h_t}{\gamma}\right), \quad (12)$$

where ρ_s is the density of the soil, h_t is the thickness of the PDZ when the soil age is t , W_0 is the lowering rate of the PDZ-CAZ boundary when there is no PDZ, and γ is a length scale that describes the decline in PDZ production as a function of PDZ thickness. There is evidence that chemical weathering fronts in the CAZ behave in a similar manner [*Burke et al.*, 2007; *Gabet et al.*, 2006; *Lebedeva et al.*, 2007], suggesting that equation (12) may also be used to describe the advance of the weathering front through parent material. By integrating equation (12) starting from zero soil thickness, we find that the soil thickness as a function of time is

$$h_t = \gamma \ln\left(\frac{\rho_r t W_0}{\rho_s \gamma} + 1\right). \quad (13)$$

Inserting equation (13) into equation (12) yields the soil production rate as a function of time:

$$P_t = \frac{\gamma \rho_s W_0}{\gamma \rho_s + t \rho_r W_0}. \quad (14)$$

Combining equations (10, 11, and 14), we find

$$M_\tau = \int_{T_s-\tau}^{T_s} \rho_r \frac{\gamma \rho_s W_0}{\gamma \rho_s + t \rho_r W_0} \exp\left(\frac{k[T_s - t]^{1+\sigma}}{1 + \sigma}\right) dt. \quad (15)$$

Figure 2 shows M_τ/M_{tot} and the mineral age density function, $\psi(\tau)$ for four minerals, quartz, potassium feldspar, plagioclase, and biotite in a soil that is 100 ka old. These plots are generated through numerical integration of equation (15). M_{tot} is calculated by integrating equation (15) from 0 to T_s . Parameter values for mineral weathering are given in Table 1.

[20] Because quartz is conservative and there is no erosion, the particle age distribution of quartz represents the history of soil production. Entrainment of material into the PDZ (often called soil production) is rapid at first because the PDZ is initially thin and then declines as time passes. Therefore, there is a greater probability of finding older quartz grains in the PDZ. Dissolution of weathering-susceptible minerals alters their particle age distribution, however. The probability of finding weathering-susceptible minerals like biotite is lowest at intermediate age. Like quartz, many weathering-susceptible minerals such as biotite are introduced into the soil in the early stages of soil formation, so there is a high probability of finding old biotite grains. The probability of finding old biotite grains is lower than that of finding old quartz grains, however, because biotite grains are more readily lost to dissolution. Conversely, the probability of finding young biotite grains is enhanced because they have not had time to undergo dissolution reactions. Thus, the probability finding very young biotite grains is greater than that of finding grains of intermediate age. Biotite, which is the mineral most susceptible to weathering in Figure 2, has the greatest probability of

young particles and lowest probability of old particles. Therefore, the mean ages of minerals within the soil increase in the following order: biotite, plagioclase, K feldspar, and quartz [Yoo and Mudd, 2008a].

3.2. Mineral Ages: Eroding Landscapes

[21] We now consider three scenarios reflecting distinct combinations of erosion and mixing for the PDZ in eroding landscapes (Figures 1b–1d).

3.2.1. Surface Erosion, No Mixing

[22] The first example is a landscape in which erosion occurs only from its surface (e.g., no creep or plug flow) and is not mixed. The natural analog would be a landscape where erosion is dominated by processes such as rainsplash or sheetwash that are only active at the surface and not within the PDZ. Here we limit our analysis to steadily eroding landscapes, where the thickness of the PDZ remains constant because the erosion rate (E is the length/time) is balanced by the soil production rate (i.e., $E = P$). By setting the P equal to the erosion rate in the soil production function (equation 12), one can calculate the thickness of the PDZ as a function of erosion rate:

$$h = -\gamma \ln(E\rho_s/W_0\rho_r). \quad (16)$$

As a denser parent material is converted into a less dense soil, the material undergoes some degree of expansion. Therefore, for the surface-lowering rate (the rate of change in the ground surface elevation) to equal the lowering of the boundary between soil and its parent material (required if the system is to remain at steady state), the rate of removal of soil, E , must be related to the surface-lowering rate by the factor ρ_r/ρ_s . In steadily eroding landscapes that are unmixed, the maximum age is equal to the turnover time: when a particle's age equals the turnover time, it has reached the surface and is eroded from the system. The turnover time in this scenario is

$$\tau_0 = \frac{-\gamma\rho_r \ln(E\rho_s/W_0\rho_r)}{E\rho_s}. \quad (17)$$

The age of minerals in the landscapes is a function of their elevation above the bottom of the PDZ: the oldest minerals are found at the shallowest depths. If the elevation of the bottom of the PDZ is defined as $z = 0$, then the age of a mineral in the soil is $\tau = z/E$. Because the maximum age of minerals is equal to the turnover time, the mass remaining with an age less than or equal to τ in the soil can be obtained as

$$M_\tau = \int_0^\tau E\rho_s \exp\left(\frac{kt^{1+\sigma}}{1+\sigma}\right) dt. \quad (18)$$

M_{tot} is calculated by integrating equation (18) from zero to τ_0 .

[23] Because of erosion and subsequent soil production, the mineral age distributions in the unmixed, eroding landscapes (Figures 3a and 3b) are fundamentally different from those in noneroding landscapes (Figure 2). The mean age of quartz in this unmixed scenario is exactly half of the turnover time (Figure 4) because the age of quartz grains are uniformly distributed from zero to the turnover time (Figure 3b).

As in the case of the noneroding landscape, chemical weathering alters the particle age distribution of other simulated minerals. Weathering-susceptible minerals lose mass as long as they remain in the weathering zone. Therefore, the probability of finding older particles is reduced relative to younger particles. However, the difference in age distributions between minerals are significantly less than in the noneroding soils (Figure 2). This is because the erosion and subsequent soil production keep the minerals' ages younger, and thus, there is less time for differences in the age distributions of different minerals to develop.

[24] The mean residence time of conservative minerals (e.g., quartz) is equal to the turnover time because these minerals are physically removed as they arrive at the soil surface. Furthermore, all conservative minerals leaving the system have the same residence time. This is demonstrated by the homogeneous age distribution of quartz in Figure 3b. However, weathering-susceptible minerals (e.g., plagioclase) leave the PDZ not only by physical erosion but also by chemical weathering.

3.2.2. Surface Erosion, Fully Mixed

[25] Here we consider a physically disturbed zone that, like the previous example, is eroded only from the surface but differs in that it is instantaneously mixed. This is clearly an idealization but is a mathematically tractable approximation of a case in which mixing occurs on a timescale much smaller than the timescale of chemical weathering (i.e., full mixing in tens to hundreds of years, which can occur in intensively bioturbated soils [Kaste *et al.*, 2007]). Just as in the unmixed case, the turnover time can be obtained by dividing the thickness of the PDZ by the erosion rate. In other words, as long as the rates of erosion are equal, the degree of mixing within the PDZ has no impact on the turnover time.

[26] Mixing does however affect the distribution of mineral ages within the PDZ. In contrast to the unmixed scenario, minerals eroded from the surface of an instantaneously mixed PDZ are not always the oldest particles: mixing can bring younger particles to the surface and eroded material can be composed of both young and old minerals. The probability of finding an old particle is lower than finding a young particle because the longer a particle stays in the PDZ the greater the chance it reaches the surface and is eroded. In fact, in a perfectly mixed reservoir it has been shown that this process, whereby older particles are less likely to remain in the reservoir, results in an exponential distribution of particle ages [Eriksson, 1971]. In addition, the mean particle age in a perfectly mixed reservoir is equal to the turnover time [Eriksson, 1971]. The fraction of total mass remaining that is of age younger than or equal to τ is then

$$\frac{M_\tau}{M_{\text{tot}}} = \int_0^\tau \frac{1}{\tau_0} \exp\left(-\frac{t}{\tau_0}\right) \exp\left(\frac{kt^{1+\sigma}}{1+\sigma}\right) dt, \quad (19)$$

and the mineral age distribution is

$$\psi(\tau) = \frac{1}{\tau_0} \exp\left(-\frac{\tau}{\tau_0}\right) \exp\left(\frac{k\tau^{1+\sigma}}{1+\sigma}\right). \quad (20)$$

The mineral age distribution of a fully mixed PDZ is shown in Figures 3c and 3d. Note the large difference in the ranges of mineral ages between the two scenarios with and without

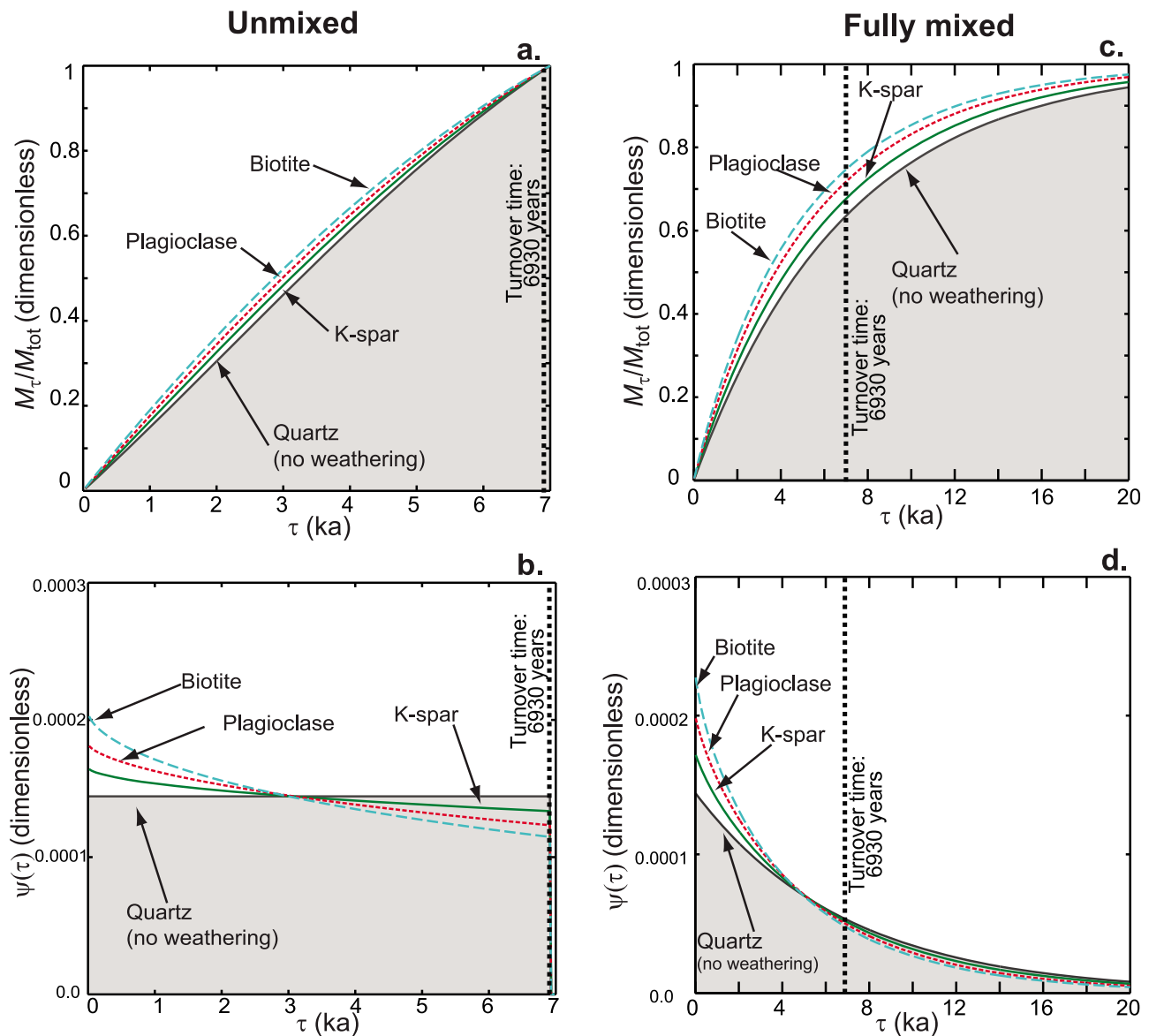


Figure 3. Fraction of mass with (a) age less than M_τ and (b) mineral age density function of an eroding, unmixed soil. Fraction of mass with (c) age less than M_τ and (d) mineral age density function of an eroding, fully mixed soil. Erosion occurs at the surface only; particles within the soil do not move downslope. Note that M_τ/M_{tot} is the cumulative density function of mineral age. The soil turnover times are indicated on the plots. Note the different temporal scale between Figures 3a and 3b and Figures 3c and 3d. The parameters used for the model simulation are $W_0 = 0.1$ mm/yr, $\gamma = 0.5$ m, $E = 0.05$ mm/yr, and the steady state soil thickness = 0.3466 m. Table 1 shows the mineral properties (all grains have starting diameter of 0.1 mm).

vertical mixing. This is despite their identical turnover times due to identical erosion rates. Such differences in the age distributions further result in significantly lengthened mean ages of minerals in the mixed PDZ (Figure 4). The mean age of quartz is equal to the turnover time in the mixed, eroding scenario. In contrast, the mean age of quartz is half of the turnover time in the unmixed, eroding scenario (Figure 4). Minerals that are more susceptible to chemical weathering are more likely to be younger than conservative minerals because as they age they lose mass by chemical weathering.

[27] For quartz, the residence time distribution is identical to the age distribution because the combination of physical

erosion at the soil surface and instant mixing within the soil results in the erosional removal of randomly selected minerals. The residence time distribution for other weathering-susceptible minerals, however, diverges from the residence time distribution of quartz because they leave weathering zone through either physical erosion or chemical weathering and because chemical weathering preferentially occurs to younger minerals in our simulation (equation 10). The difference in the residence time distribution and the particle age distribution, therefore, represents the age distribution of minerals that are lost from the soil via chemical weathering (Figure 5).

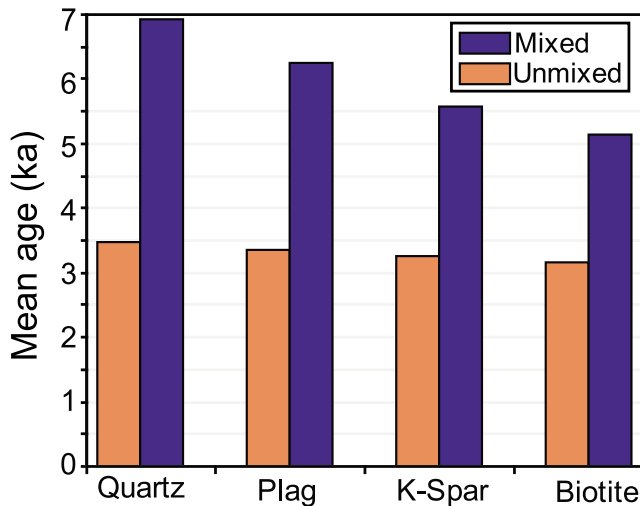


Figure 4. Mean ages of selected minerals for mixed and unmixed scenarios. Parameters are the same as in Figure 3. Turnover time is the same in both cases: 6.93 ka.

3.2.3. No Surface Erosion; Creep Transport Only

[28] Finally, consider material in the physically disturbed zone that only erodes through creep-like processes. In such hillslopes, material moves due to a combination of biophysical perturbations and gravity [Kirkby, 1967; Heimsath *et al.*, 2002; Roering, 2004; Furbish *et al.*, 2009]. This situation is common in landscapes where soils are porous enough to preclude overland flow [e.g., Montgomery *et al.*, 1997] or where vegetation such as grasses forms a protective layer that prevents erosion from the surface [e.g., Prosser *et al.*, 1995].

[29] Creeping material moves downslope within the PDZ profile (Figure 1), and the flux of this material is, by definition, equal to

$$q = vh, \quad (21)$$

where v is the mean particle velocity and q is a volumetric flux per unit width. In a steadily eroding hillslope where either mass loss due to chemical weathering is small compared to physical transport or chemical weathering leads to greater porosity, the volumetric flux will equal the integral of all material eroded upslope of some point on the hillslope such that $q = Ex$ where x is the distance from the divide. The velocity of minerals within the PDZ can be stated as $v = \partial x / \partial t$ [Mudd and Furbish, 2006] so that

$$\frac{\partial x}{\partial t} = \frac{Ex}{h}. \quad (22)$$

[30] Noting that $E/h = 1/\tau_0$, integration of equation (22) yields an exponential function describing the time it takes a particle to move some distance $x-x_0$ down the hillslope. Mudd and Furbish [2006] demonstrated that the probability distribution of mineral ages at any location on a creeping hillslope takes an exponential distribution; that is, there is a much higher probability of finding young particles than old. This is because the probability of particle source locations is uniform due to spatially uniform erosion rates and because

particles are moving with greater velocity as they move downslope. Particle velocity increases downslope because as one moves away from the divide more sediment must be removed from the hillslope to maintain steady state, but the thickness of the PDZ does not change because soil production must also remain constant. The result is that old particles from the divide move slower than particles originating from downslope, resulting in a greater number of young particles than old particles at any point on the slope. Thus, the particle age and residence time distributions of a creeping soil are identical to those in the perfectly mixed eroding soil investigated in section 3.2.2. Note that in a purely creeping soil minerals that survive dissolution reactions must exit from the base of the hillslope (i.e., they are not eroded from the surface of the hillslope). The analysis presented here for the creeping scenario makes no assumption of mixing intensity: mineral age is exponentially distributed in a creeping PDZ as a consequence of sediment transport, regardless of the mixing intensity. Thus, the age and residence time distributions in a creeping PDZ are identical to those in a fully mixed PDZ that experiences erosion only at its surface whether the creeping PDZ is mixed or not.

3.2.4. Comparison of Erosion Scenarios

[31] Figure 6 compares different measures of time for quartz in unmixed and fully mixed soils as a function of erosion rate. As discussed above, creeping material behaves identically to PDZ material that only erodes from the surface and is fully mixed. The mean age of quartz in the unmixed scenario is exactly half of the mean residence time or turnover time. This is in direct contrast to quartz in fully

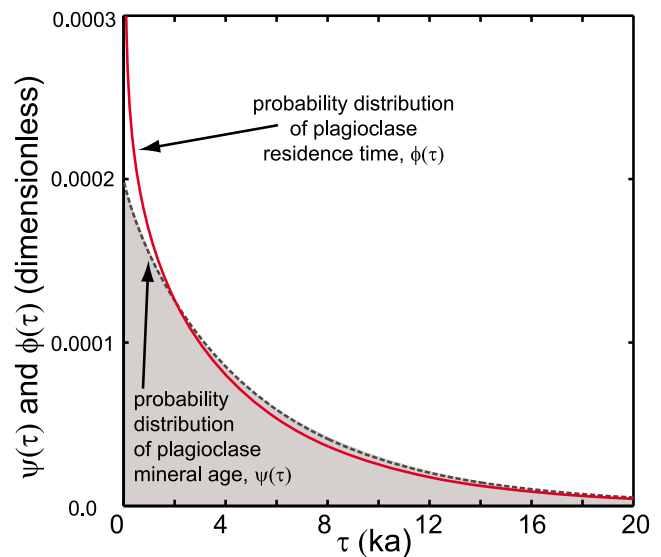


Figure 5. Mineral age distribution and residence time distribution for plagioclase in a fully mixed soil. The residence time records the distribution of times at which minerals leave the system and therefore includes mass lost to both physical erosion and chemical weathering. The difference between the two curves represents the distribution of chemical weathering as a function of age; younger particles weather more quickly so the residence time distribution is skewed toward younger ages. The parameters used for the model simulation are identical to the ones in the Figure 3.

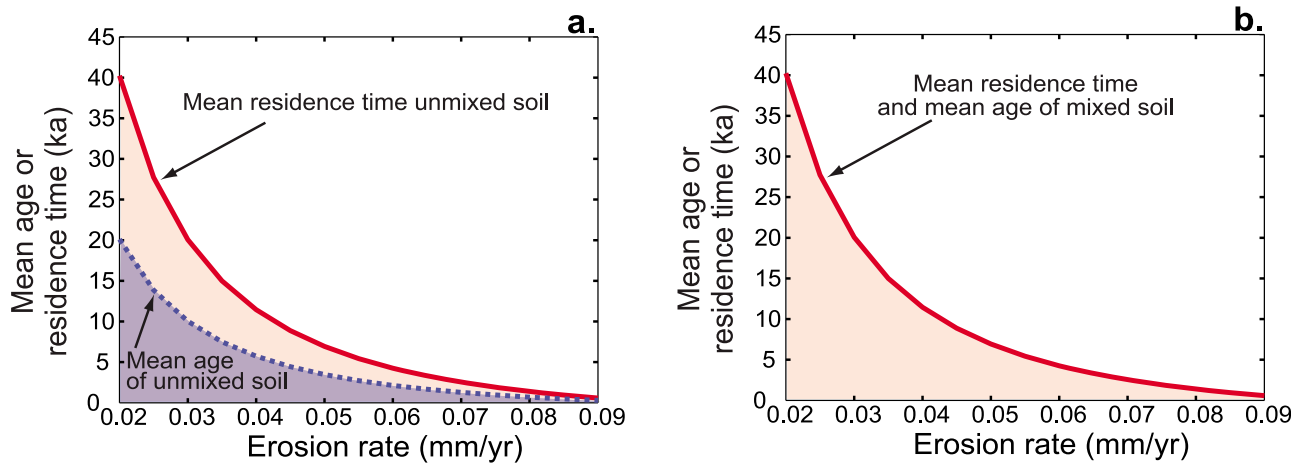


Figure 6. (a) Mean age and mean residence time of quartz in a landscape where mixing is negligible. (b) Mean age and mean residence time of quartz in a landscape with instantaneous mixing. Both mean age and residence time of quartz lie on the same curve in this scenario. The parameters are the same as in Figure 3.

mixed or creeping scenarios where both the distributions and means of residence time and mineral age are the same. All of these measures of time nonlinearly increase with decreasing erosion rate.

[32] Despite the similarity in turnover times in the mixed, unmixed, and creeping scenarios, chemical weathering rates and relative chemical depletion will be different because of the differences in mineral age and residence time distributions. We provide an example. The relative depletion of minerals in and leaving the PDZ are shown in Figure 7. The mean age of unmixed minerals is less than the mean age of fully mixed minerals (Figure 4). Therefore, unmixed minerals within the PDZ have less time to weather and are thus less chemically depleted, if averaged throughout the PDZ, than mixed minerals. Because unmixed minerals are younger than their mixed counterparts their chemical weathering rate is greater.

[33] The chemical weathering rate of a steadily eroding PDZ must be equal to the rate that mass enters the PDZ minus the rate it is physically eroded [Waldbauer and Chamberlin, 2005; Hren et al., 2007; Gabet and Mudd, 2009]; thus, if more depleted material is eroded from the PDZ, the chemical weathering rate will be greater, or vice versa. This is confirmed by Figure 7: unmixed minerals that are eroded are more depleted than their mixed counterparts. In a landscape where mixing is vigorous, the material leaving the hillslope is from the same age population of that in the hillslope, but in a landscape where mixing is negligible, material being eroded is much older and, therefore, more depleted than the material present on the hillslope. From this result, we learn that if chemical weathering rates are to be determined using a solid-state geochemical mass balance approach [e.g., Riebe et al., 2001], it is crucial to quantify the relative depletion of material leaving the PDZ and not the material that is within the PDZ. That is, one

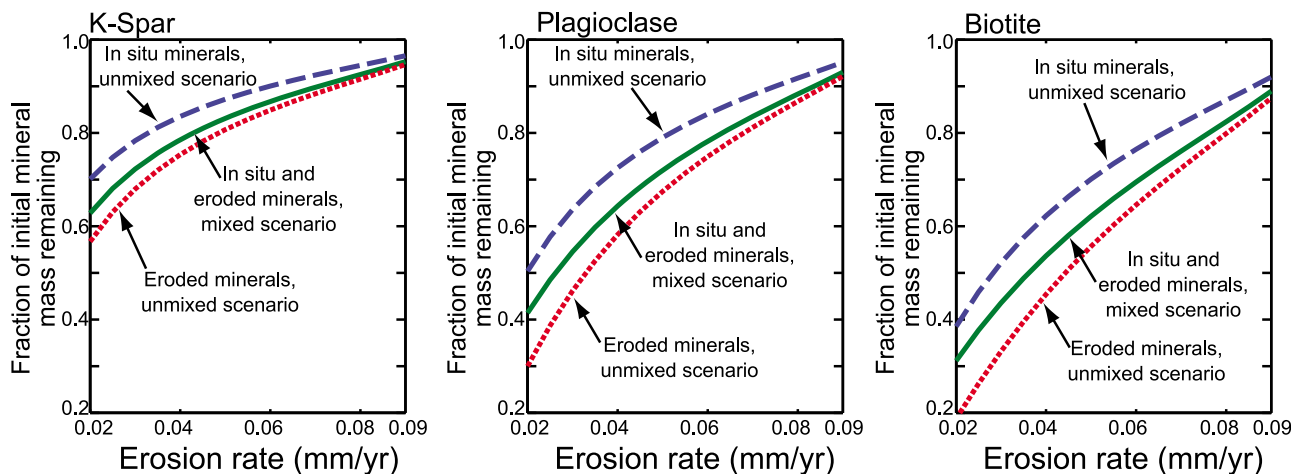


Figure 7. Fraction of minerals remaining in a soil for three mineral species in different erosion scenarios. All three scenarios feature steady soil thickness where soil production is balanced by chemical weathering and physical erosion. The fraction remaining is the total mass of a mineral species M_{tot} , divided by the total mass of that species introduced into the soil via soil production.

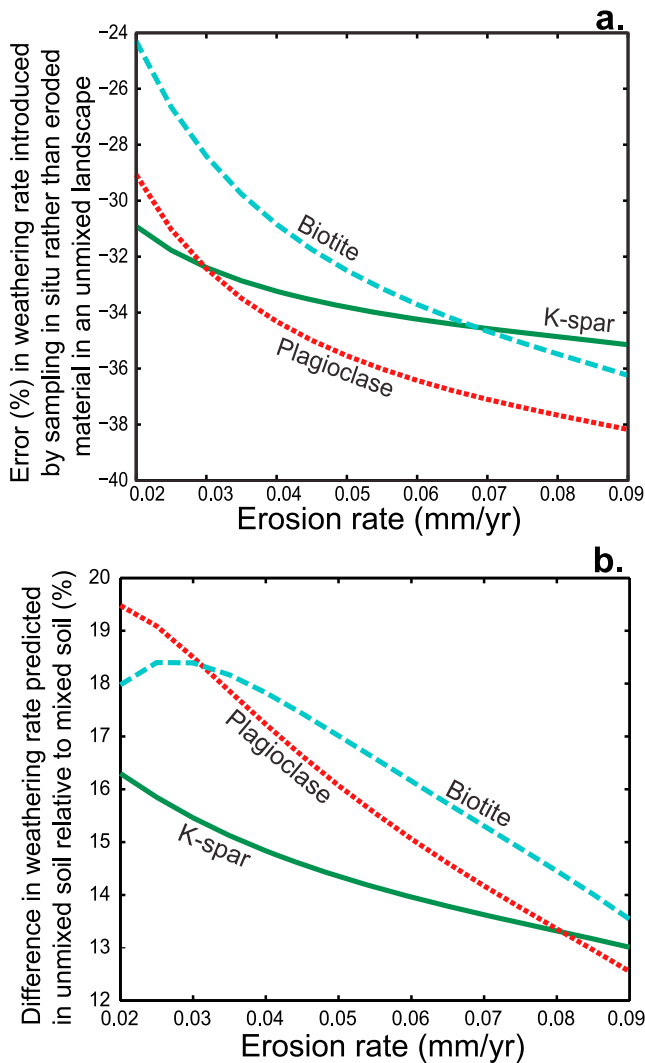


Figure 8. (a) Error in weathering rates that would result if they were calculated by sampling in situ hillslope material rather than material leaving hillslope in a negligibly mixed landscape. In situ material is less depleted than material leaving the hillslope so sampling in situ material would result in an underestimate of the chemical weathering rate. (b) The percent difference in weathering rate between a landscape in which the PDZ is negligibly mixed and one in which the PDZ is perfectly mixed, all else equal. Landscapes with negligibly mixed PDZs have greater chemical weathering rates than mixed landscapes. For both Figures 8a and 8b, model parameters are the same as in Figure 3.

should sample material in the fluvial system leaving a hillslope rather than the material present on the hillslope. If a mass balance approach is used to quantify chemical weathering rates in landscapes with minimal mixing and mineral depletion is measured using minerals present rather than minerals being eroded, an erroneous estimate of relatively slow weathering in relation to a landscape with vigorous mixing would result (Figure 8a). In a landscape with minimal mixing, calculating weathering rates based on the chemical depletion of material within the hillslope rather

than material leaving it may result in an underestimate of the weathering rate by, in some cases, more than 30% (Figure 8a). There are also differences in weathering rates in landscapes that have vigorous or negligible mixing, all else being equal: weathering rates are greater in landscapes with negligible mixing by, in some cases almost 20% (Figure 8b). Although this exercise does not consider scenarios in which weathering rates in the PDZ are a strong function of depth, this result highlights that mixing intensity, independent of erosion rates, may further complicate our understanding of the landscape scale variation in chemical weathering rates.

4. Conclusions

[34] A key challenge in translating laboratory measurements of mineral weathering to natural settings is defining and quantifying time [e.g., *White and Brantley, 2003; Brantley, 2008; Yoo and Mudd, 2008a*]. Dissolution rates are quantified as the mass lost over time, but measures of time and the terms used to describe them have been inconsistently used in the geochemical and geomorphic literature. We have analyzed time in natural weathering environments by applying the well-established principals of reservoir theory. Reservoir theory identifies three distinct measures of time: turnover time, age, and residence time. We have quantified these measures of time for soils in a variety of landscapes, both eroding and noneroding and with the presence and absence of mixing within the soils. In most prior research only the turnover time, which has in the past been referred to as residence time, and soil age have been quantified: our results show that these two measures give an incomplete picture of the dynamics of the weathering zone.

[35] Application of reservoir theory to both eroding and noneroding landscapes requires knowledge of soil production (defined as the rate at which material is entrained into the physically disturbed zone, or PDZ), transport, soil mixing, and dissolution processes. The ability to calculate mineral ages, residence times, and turnover time for the minerals within weathering systems is limited by the uncertainties involved in quantifying these processes. However, reservoir theory, in treating the weathering zone as an open system through which materials flow, allows us to link geochemical and geomorphic processes in a quantitative framework that can bridge the scale of a mineral grain to a landscape. The mean and distribution of mineral ages in the physically disturbed portion of a soil, which are driven primarily by geomorphic processes, can be related to empirical observations of mineral surface morphologies such as their degree of weathering. By combining field observations with calculated mineral ages, one can relate short-term behavior of minerals, which have been constrained by laboratory experiments to the timescales important for soil formation, i.e., the time it takes a weathering profile to achieve its present geochemical character. We have calculated mineral ages based on rates of soil production and erosion that have been constrained by previous geomorphic studies. These ages span hundreds to millions of years, which provides an unprecedented opportunity to quantitatively understand the mineral weathering as a function of time in the weathering environment.

[36] Lastly, while the soil turnover time (i.e., soil residence time in the preceding literature) has been implicitly or

explicitly considered as the time length that minerals are chemically weathered in soils on eroding hillslopes [e.g., Riebe *et al.*, 2001; Almond *et al.*, 2007; Yoo *et al.*, 2007], our analysis shows that soils with same turnover time and mineralogical compositions can still have different chemical weathering rates depending on their internal mixing dynamics. This is because mixing dynamics, together with erosion process, determines mineral age in soils. Traditionally, it has been thought that soil chemical weathering rates are limited by either the rate of mineral supply, which is generally related to tectonics, or geochemical equilibrium between minerals and soil water, which is typically associated with climate [West *et al.*, 2005]. Our simulations, however, propose another possibility: different internal mixing regimes within soils may lead to significantly different chemical weathering rates under identical erosion rates and hydrological environments.

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