
Peer reviewed version

Link to published version (if available):
10.1016/B978-0-08-095975-7.00504-0

Link to publication record in Explore Bristol Research
PDF-document

University of Bristol - Explore Bristol Research

General rights

This document is made available in accordance with publisher policies. Please cite only the published version using the reference above. Full terms of use are available: http://www(bristol.ac.uk/pure/about/ebr-terms
5.4 Natural Weathering Rates of Silicate Minerals

A. F. White

U. S. Geological Survey, Menlo Park, CA, USA

and

H. L. Buss

School of Earth Sciences

University of Bristol, Bristol, UK
Contacts:
Art White
U. S. Geological Survey
MS 420
345 Middlefield Rd.
Menlo Park, CA 94025
Phone: 650-329-4519
Fax 650-329-4538
afwhite@usgs.gov

Heather Buss
School of Earth Sciences
University of Bristol
Wills Memorial Building
Queen’s Road
Bristol, BS8 1RJ, UK
h.buss@bristol.ac.uk
SYNOPSIS

This chapter presents 1) the development of rates that quantitatively describe silicate mineral and rock weathering, 2) a summary of the available literature rate data for the weathering of several common silicate minerals, and 3) a discussion of the chemical, physical and hydrologic processes that control silicate mineral weathering at the Earth’s surface. Quantitative rates of weathering are important in understanding reaction mechanisms and in addressing a number of economic and environmental issues. Mass change, defined in terms of elements, isotopes or mineral abundances is determined from either solid state (soil, regolith, rock) or solute (pore water, groundwater, surface water) compositions. Solid-state mass differences reflect weathering over geologic time scales while solute compositions reflect the residence time of the water. These mass losses or gains are normalized to surface area defined on a geographic, volumetric or mineral-specific basis. The advantages of this approach are that such rates are related to reaction mechanisms and can be used as predictive tools in estimating how weathering will behave under various environmental conditions.

KEYWORDS: profile, regolith, silicate, soil, weathering rates
**NOMENCLATURE**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b_{\text{solid}} )</td>
<td>Solid weathering gradient (m kg mole(^{-1}))</td>
</tr>
<tr>
<td>( b_{\text{solute}} )</td>
<td>Solute weathering gradient (m L mole(^{-1}))</td>
</tr>
<tr>
<td>( c )</td>
<td>Concentration of weatherable component in solute (molar)</td>
</tr>
<tr>
<td>( C_{j,w} )</td>
<td>Final concentration of weatherable component ( j ) in regolith (moles m(^{-3}))</td>
</tr>
<tr>
<td>( C_{j,p} )</td>
<td>Initial concentration of weatherable component ( j ) in protolith (moles m(^{-3}))</td>
</tr>
<tr>
<td>( C_{i,w} )</td>
<td>Final concentration of inert component ( i ) in regolith (moles m(^{-3}))</td>
</tr>
<tr>
<td>( C_{i,p} )</td>
<td>Initial concentration of inert component ( i ) in protolith (moles m(^{-3}))</td>
</tr>
<tr>
<td>( d )</td>
<td>Mineral grain diameter (m)</td>
</tr>
<tr>
<td>( D )</td>
<td>Total denudation rate (m s(^{-1}))</td>
</tr>
<tr>
<td>( D_j )</td>
<td>Diffusion coefficient (m(^2) s(^{-1}))</td>
</tr>
<tr>
<td>( E )</td>
<td>Physical erosion rate (m s(^{-1}))</td>
</tr>
<tr>
<td>( E_a )</td>
<td>Activation energy (kJ mole(^{-1}))</td>
</tr>
<tr>
<td>( \Delta G )</td>
<td>Excess free energy of reaction (kJ mole(^{-1}))</td>
</tr>
<tr>
<td>( \Delta H )</td>
<td>Enthalpy of reaction (kJ mole(^{-1}))</td>
</tr>
<tr>
<td>( VH )</td>
<td>Hydraulic gradient (m m(^{-1}))</td>
</tr>
<tr>
<td>( h_g )</td>
<td>Gravitational head (m m(^{-1}))</td>
</tr>
<tr>
<td>( h_p )</td>
<td>Pressure head (m m(^{-1}))</td>
</tr>
<tr>
<td>( \text{IAP} )</td>
<td>Ionic activity product</td>
</tr>
<tr>
<td>( K_s )</td>
<td>Mineral solubility product</td>
</tr>
<tr>
<td>( K_m )</td>
<td>Hydraulic conductivity (m s(^{-1}))</td>
</tr>
<tr>
<td>( k )</td>
<td>Intrinsic rate constant</td>
</tr>
<tr>
<td>( \Delta M )</td>
<td>Change in mass due to weathering (moles)</td>
</tr>
</tbody>
</table>
m_j  Atomic wt. of component j (g)
P  Annual precipitation (m)
q_h  Flux density of water (m s^{-1})
Q  Solute flux (moles ha^{-1} yr^{-1})
R_{solid}  Reaction rate based on solid concentrations (moles m^{-2} s^{-1})
R_{solute}  Reaction rate based on solute concentrations (moles m^{-2} s^{-1})
R'  Gas constant (joules mole^{-1} °K^{-1})
S  Surface area (m^2)
S_s  Specific surface area (m^2 g^{-1})
S_v  Volumetric surface area (m^2 m^{-3})
T  Temperature (°K)
t  Duration of weathering (s)
V_s  Volume of solute
V_m  Molar volume (m^3)
W  Chemical weathering flux (m s^{-1})
z  Distance (m)
β  Stoichiometric coefficient
ε  Volumetric strain
ϕ  Porosity (m^3 m^{-3})
λ  Surface roughness (m^2 m^{-2})
ν  Solute weathering velocity (m s^{-1})
ρ  Specific mineral density (m^3 g^{-1})
ρ_p  Density of regolith (g cm^{-3})
$\rho_w$  Density of protolith (g cm$^{-3}$)

$\tau_j$  Mass transfer coefficient

$\omega$  Solid state weathering velocity (m s$^{-1}$)

$\Omega$  Thermodynamic saturation state
TABLE OF CONTENTS

5.04.1 INTRODUCTION
5.04.2 DEFINING NATURAL WEATHERING RATES
5.04.3 MASS CHANGES RELATED TO CHEMICAL WEATHERING
   5.04.3.1 Bulk Compositional Changes in Regoliths
      5.04.3.1.1 Weathering Indices
      5.04.3.1.2 Mass Transfer
      5.04.3.1.3 Profile categories
      5.04.3.1.4 Time evolution of profiles
      5.04.3.1.5 Utilization of Soil Chronosequences
      5.04.3.1.6 Steady-state denudation and weathering-profile development
   5.04.3.2 Changes in Solute Compositions
      5.04.3.2.1 Characterization of fluid transport
      5.04.3.2.2 Weathering based on solutes in soils
      5.04.3.2.3 Weathering based on solutes in groundwater
      5.04.3.2.4 Weathering based on surface water solutes
5.04.4 NORMALIZATION OF WEATHERING TO SURFACE AREA
   5.04.4.1 Definitions of Natural Surface Areas
   5.04.4.2 Measurements of Specific Surfaces Areas
   5.04.4.3 Surface Roughness
5.04.5 TABULATIONS OF WEATHERING RATES OF SOME COMMON SILICATE MINERALS
   5.04.5.1 Elemental Weathering Fluxes
5.04.5.2 Mineral Weathering Fluxes

5.04.5.3 Specific Mineral Weathering Rates

5.04.6. TIME AS A FACTOR IN NATURAL WEATHERING

5.04.1 Comparison of Contemporary and Geologic Rates

5.04.7. FACTORS INFLUENCING NATURAL WEATHERING RATES

5.04.7.1 Mineral Weatherability

5.04.7.2 Solute Chemistry and Saturation States

5.04.7.3 Coupling the Effect of Hydrology and Chemical Weathering

5.04.7.3.1 Low permeability

5.04.7.3.2 High permeability

5.04.7.4 The Role of Climate on Chemical Weathering

5.04.7.4.1 Temperature

5.04.7.4.2 Precipitation and recharge

5.04.7.4.3 Coupling climate effects

5.04.7.5 The Role of Physical Weathering

5.04.8 SUMMARY
5.04.1 INTRODUCTION

Silicates constitute more than 90% of the rocks exposed in the earth’s land masses (Garrels and Mackenzie, 1971). Most primary minerals comprising these rocks are thermodynamically unstable at surface pressure/temperature conditions and are therefore susceptible to chemical weathering. Such weathering has long been of interest in the natural sciences. Hartt (1853) correctly attributed chemical weathering to “the efficacy of water containing carbonic acid in promoting the decomposition of igneous rocks”. Antecedent to the recent interest in the role of vegetation on chemical weathering, Belt (1874) observed that the most intense weathering of rocks in tropical Nicaragua was confined to forested regions. He attributed this effect to “the percolation through rocks of rain water charged with a little acid from decomposing vegetation”. Chamberlin (1899) proposed that that enhanced rates of chemical weathering associated with major mountain building episodes in the Earth’s history resulted in a drawdown of atmospheric CO₂ that led to periods of global cooling. Many of the major characteristics of chemical weathering had been described when Merrill (1906) published the groundbreaking volume Rocks, Rock Weathering and Soils.

The major advances since that time, particularly during the last several decades, have centered on understanding the fundamental chemical, hydrologic and biologic processes that constitute Earth’s “weathering engine” and in establishing quantitative weathering rates (Figure 1). This research has been driven by the importance of chemical weathering to a number environmentally and economically important issues. Most weathering occurs within the “critical zone”, which is the external layer of the Earth from the vegetation canopy to fractured bedrock. This zone sustains most terrestrial life on the planet, yet natural and human-related processes perturb and threaten the Critical Zone worldwide. Undoubtedly, the most significant aspect of chemical weathering is the breakdown of rocks to form soils, a process that creates the Critical Zone and makes life possible on the surface of the earth (Brantley et al., 2006). The availability of many soil macronutrients such as K, Ca Mg, and PO₄ is directly related to the rate at which primary minerals weather. Often such nutrient balances are upset by anthropogenic activities. For example, Huntington (2000) showed that extensive timber harvesting in the southeastern forests
of the United States, which are underlain by intensely weathered saprolites, produces net Ca exports that exceed inputs from weathering, thus creating a long-term regional problem in forest management.

**Figure 1 Near Here**

The role of chemical weathering has long been recognized in economic geology. Tropical bauxites, which account for most of the world’s Al ores, are typical examples of residual concentration of silicate rocks by chemical weathering of over long time periods (Samma, 1986). Weathering of ultramafic silicates such as peridotites form residual lateritic deposits that contain significant deposits of Ni and Co. Ores generated by chemical mobilization include uranium deposits that are produced by weathering of granitic rocks under oxic conditions and subsequent concentration by sorption and precipitation (Misra, 2000).

Over the last several decades, estimating rates of silicate weathering has become important in addressing new environmental issues. Acidification of soils, rivers and lakes has become a major concern in many parts of North America and Europe. Areas at particular risk are uplands where silicate bedrock, resistant to chemical weathering, is overlain by thin organic-rich soils (Driscoll et al., 1988). Although atmospheric deposition is the most important factor in watershed acidification, land use practices, such as conifer reforestation, also create acidification problems (Farley and Werritty, 1989). In such environments, silicate hydrolysis reactions are the principal buffer against acidification. As pointed out by Drever and Clow (1995), a reasonable environmental objective is to decrease the inputs of acidity such that they are equal to or less than the rate of neutralization by weathering in sensitive watersheds.

The intensive interest in past and present global climate change has renewed efforts to understand and quantitative feedback mechanisms between climate and chemical weathering. On time scales longer than a million years, atmospheric CO₂ levels have been primarily controlled by the balance between the rate of volcanic inputs from the Earth’s interior and the rate of uptake through chemical weathering of silicates at the Earth’s surface (Ruddiman, 1997). Weathering is proposed as the principal moderator in controlling large increases and decreases in global temperature and precipitation through the greenhouse effects of CO₂ over geologic time (Berner and
Weathering of paleosols has also been used as an indicator of changes in Archean atmospheric CO2 and O2 levels (Ohmoto, 1996; Rye and Holland, 1998).

5.04.2 DEFINING NATURAL WEATHERING RATES

Chemical weathering is characterized in either qualitative or quantitative terms. Qualitative approaches entail comparing the relative weathering of different minerals or the weathering of the same mineral in different environments. Early observations by Goldich (1938) showed that the weathering sequence of igneous rocks in the field was the reverse of Bowen’s reaction series that ranked minerals in the order of crystallization from magmas. Thermodynamic and kinetic considerations have added new dimensions to characterizing the relative weatherability of various minerals and rocks (reviews in Brantley et al., 2007). Silicate weathering has long been recognized as exhibiting consistent trends with time and climate (Jenny, 1941; Ollier, 1984). Such studies provide valuable insights into weathering processes and into the influence of environmental conditions such as climate, vegetation and geomorphology. A number of these issues are discussed elsewhere in this volume (Amundson, this volume; Granger and Riebe, this volume).

The primary focus of this chapter is on the development of rates that quantitatively describe silicate mineral and rock weathering. The advantages of this approach are that such rates are related to reaction mechanisms and can be used as predictive tools in estimating how weathering will behave under various environmental conditions.

The weathering rate \( R \) (moles \( m^{-2} \cdot s^{-1} \)) of a primary silicate mineral is commonly defined by the relationship

\[
R = \frac{\Delta M}{S \cdot t}
\]

where \( \Delta M \) (moles) is the solid or solute mass change due to weathering, \( S \) (m\(^2\)) is the total surface area involved and \( t \) (s) is the duration of the reaction. The weathering rate is therefore equivalent to a chemical flux. Much of the following discussion will center on how the terms on the right side of Equation 1 are determined and quantified. This discussion will focus on silicates but is applicable, in various degrees, to other types of minerals, such as carbonates, sulfates and sulfides that commonly weather at significantly faster rates.
An important feature of silicate weathering is the extremely large spatial and temporal scales over which the parameters describing weathering are measured (Equation 1). Natural weathering can be characterized by changes in microscopic surface morphologies of mineral grains, by solid and solute changes in soil profiles, from solute fluxes in small watersheds and large river basins and by continental and global-scale element cycles. Clearly, the degree to which individual weathering parameters are characterized depends strongly on the magnitude of these scales. Several other chapters in this volume deal in greater detail with some of these specific weathering environments, i.e., soils (Amundson, this volume), glacial environments (Tranter, this volume) watersheds (Meybeck, 2004) and river systems (Viers et al., this volume).

5.04.3 MASS CHANGES RELATED TO CHEMICAL WEATHERING

Silicate weathering involves hydrolysis reactions that consume reactant species, i.e., primary minerals and protons and form weathering products, i.e., solute species and secondary minerals. A typical hydrolysis reaction is the weathering of albite feldspar to form kaolinite

\[ 2NaAlSi_3O_8 + 2H^+ + H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 4SiO_2 \]  

which consumes hydrogen ions and water and produces kaolinite and solute Na and SiO_2. For a more detailed discussion of the reaction mechanisms of silicate weathering, the reader is referred to Brantley et al. (2007), Oelkers and Schott (2009) and Brantley and Olsen (this volume).

The rate of weathering is reflected by the mass change $\Delta M$ with time of any of the individual components in a reaction if the overall stoichiometry is known. The consumption of hydrogen ions can, in principle, determine the rate of plagioclase reaction (Equation 2). However such measurements are difficult due to the many sources and sinks of hydrogen ion in the weathering environment, e.g. CO_2, organic acids and ion exchange reactions. Use of secondary minerals to define weathering rates is also difficult due to compositional heterogeneities and non-conservative behavior. In Equation 2, Al is completely immobilized in kaolinite during plagioclase weathering. However, in low pH and/or organic-rich weathering environments, Al exhibits significant mobility and the quantity of kaolinite produced no longer directly reflects the amount of plagioclase that has reacted.
Most weathering rate studies have focused on measuring decreases in the solid-state reactant and/or increases in one or more of the mobile solute products. Examples of such changes due to weathering are shown in Figure 2 for solid-state and pore water Na distributions with depth in a 160-kyr-old marine terrace in California (White et al., 2008). Mineralogical analyses indicate that significant Na is contained only in plagioclase. Therefore, both the decrease in solid-state Na with decreasing depth and the increase in solute Na with increasing depth can be used to define the rate of plagioclase weathering (Equation 2).

**Figure 2. Near Here**

The solute and solid state Na distributions with regolith depth shown in Figure 2 constitute weathering profiles. Ideally, fully developed weathering profiles consist of three segments (Figure 3). A vertical segment at shallow depths indicates complete depletion of a dissolving mineral. The vertical segment at the greatest depths corresponds to the unweathered protolith. Composition gradients at intermediate depths for the solute, $b_{solute}$, and for the solid, $b_{solid}$ (White et al. 2002; 2008) define the reaction front (also called the weathering front) between the end-member conditions (represented by the vertical segments). The solute gradient reflects the accumulation of dissolved weathering products (Figure 3a) while the solid gradient in reflects decreasing concentrations of residual minerals (Figure 3b).

**Figure 3 Near Here**

The weathering rates $R_{solute}$ and $R_{solid}$ (mol m$^{-2}$ s$^{-1}$) in Figure 3 are mass fluxes normalized to the volumetric surface area of a mineral phase $S_v$ (m$^{-3}$). Over short fluid residence times and under constant hydrologic conditions, the position of the solute weathering front remains spatially fixed within a weathering profile (Figure 3a). In contrast, the solid state weathering front progressively moves downward into the protolith. In Figure 3, the solute and solid weathering gradients can be thought of as balances between mineral weathering rates $R_{solute}$ and $R_{solid}$, and the solute and solid weathering velocities $\nu$ and $\omega$ (m s$^{-1}$). Solute and solid gradients shown as solid lines in Figure 3 are linear approximations of the actual weathering fronts, which are more commonly represented by the sigmoidal dashed curves.

Mineral weathering rates are calculated from the weathering velocities and gradients, shown schematically in Figure 3, as follows (White, 2002; 2009)
\[ R_{\text{solute}} = \frac{q_h}{b_{\text{solute}} \beta s_p} \]  
\[ R_{\text{solid}} = \frac{\omega}{b_{\text{solid}} \beta s_{15}} \]

Here, \( \beta \) is the stoichiometric coefficient of the elemental concentrations in the mineral. The hydrologic flux \( q_h \) (m s\(^{-1}\)) is equivalent to the solute velocity \( \nu \) (Equation 3) while the solid-state weathering velocity \( \omega \) (m s\(^{-1}\)) defines the vertical propagation rate of a weathering front into the protolith (Equation 4). With a lack of physical denudation, the solid-state weathering velocity \( \omega \) also defines the rate at which weathering fronts retreat below the soil surface. Solute and solid weathering gradients develop over very different time spans. Solute gradients are produced over the residence times of pore waters and thus reflect contemporary weathering rates. Solid-state gradients reflect the cumulative weathering history, typically on the order of thousands to millions of years. In addition, the absolute mass change with depth per unit volume is significantly greater in the solid profile than in the solute profile such that \( b_{\text{solute}} >> b_{\text{solid}} \).

Increasing the weathering rate produces a shallower weathering gradient in which a measured solid or solute component, such as Na (Figure 2), increases more rapidly with depth. Increasing weathering velocity, due to the rate at which weathering front or the pore water moves through the profile steepens the weathering gradient. The slope of these gradients, measured under field conditions (Figure 3), can be converted to weathering rates in combination with additional physical and chemical parameters (White, 2002, 2009).

Defining the stoichiometry of the weathering reaction is often more difficult than suggested by plagioclase weathering (Equation 2). The first stage of biotite weathering, for example, involves the oxidation of ferrous atoms and the concurrent release of K to form oxybiotite (Amonette et al., 1988; Buss et al., 2008). Depending on the weathering environment, biotite subsequently undergoes direct transformation to kaolinite with congruent release of Mg (Murphy et al., 1998) or it can weather to vermiculite with Mg partially retained in the solid (Fordham, 1990).
Therefore, knowledge of the specific reaction pathway is required in order to define the rate of mineral weathering.

5.04.3.1. Bulk Compositional Changes in Regoliths

In this chapter, we define regolith as disaggregated, weathered material including soil, sediment and or saprolite with overlies bedrock or protolith. Regolith may differ from its parent material in terms of mass, volume, and/or relative abundance of elements and minerals. *Weathering indices* are commonly applied to regoliths to describe relative degrees of weathering in terms of elemental ratios.

5.04.3.1.1. Weathering Indices

Elemental ratios have long been used to characterize weathering intensities in regolith (Merrill, 1906; Jenny, 1941). They commonly involve major element oxides and are used to characterize soil fertility, the formation and cycling of siliclastic sediments, the impact of climate on bedrock weathering, and as indicators of the physical and engineering properties of regolith (Delvaux et al., 1989; Nesbitt et al., 1996; Duzgoren-Aydin et al., 2002; Price and Velbel, 2003).

Such ratios most commonly compare the concentration of one or more mobile element $C_{j,w}$ against one or more immobile elements $C_{i,w}$ to define a weathering index $I_w$

$$I_w = \frac{\sum_{0}^{n} C_{j,w}}{\sum_{0}^{n} C_{i,w}}$$

Important criteria considered in evaluating the usefulness of weathering indices are: (1) ease of use and involvement of commonly measured elements, (2) incorporation of elements with a large range of mobilities in the weathering environment, (3) variability produced by weathering is greater than the heterogeneity of the parent material and (4) applicability to a wide range of rock types (Price and Velbel, 2003).

**Table 1 Near Here**
Table 1 contains a subset of commonly used weathering indices (Duzgoren-Aydin et al., 2002; Price and Velbel, 2003). Group I indices treat silica as a mobile oxide which is ratioed against one or more major element oxides that are considered immobile, i.e., Al$_2$O$_3$, Fe$_2$O$_3$ and/or TiO$_2$. Group II indices describe major base cations ratioed against the same major immobile oxides and, finally, the Group III indices consider only the abundances of the mobile element oxides with numerical factors assigned to each cation based on its ionic field strength, a measure of weathering susceptibility (Parker, 1970).

An example of the application of weathering indices listed in Table 1 is used to evaluate basalt weathering in a regolith developed on the Hawi flow on the big island of Hawaii based on oxides reported by Chadwick et al. (2003). As indicated in Figure 4, all three groups of weathering indices exhibit comparable patterns with regolith depth. The RU index approaches a value of three at the maximum depth which is indicative of the Si/Al ratio of fresh basalt (Figure 4). At shallow depth, this ratio diminishes to near one indicating that significant Si has been mobilized. The CIA, CIW and PIA ratios at depth approach a value of 50, which is indicative of fresh bedrock. At shallow depth, these indices approach 100 which is representative of intensive chemical weathering. This agreement supports a major assumption in the application of Group I and II indices that Al$_2$O$_3$, the most abundant element next to SiO$_2$ is relatively immobile during weathering. The WP index directly reflects the extent of this base cation loss.

Figure 4 Near Here.

The best correlation between all the weathering indices occurs when the protolith is composed exclusively of readily weatherable minerals such as in basalt (Figure 4). The greater differences in the weatherability of various minerals in rocks such as granite, the greater will be the difference in various weathering indices. For example although Si is contained in weatherable aluminosilicates in basalts, the Group I indices are ineffective in characterizing granitic saprolite weathering due to the stability of quartz. However, in more intensively weathered granitic profiles such as laterites, SiO$_2$ in quartz is mobile and the Group I indices are more effective indicators of weathering (Beauvais, 1999).

In deep regoliths, Al$_2$O$_3$ released from primary silicates is immobile, being precipitated in secondary minerals, principally clays. However, in relatively shallow soils, such as spodosols,
with acidic conditions and/or with high organic contents, significant Al₂O₃ is mobilized (Driscoll et al., 1985). Similarly, Fe₂O₃ is considered an immobile component in some indices (JE, Table 1) due to the retention of Fe in secondary phases. However, under reducing weathering conditions, ferric iron is converted to ferrous iron and becomes much more mobile (Price and Velbel, 2003).

In addition to major elemental ratios discussed above, other weathering indices incorporate trace elements such as lanthanides (rare earths) and isotopes such as Nd and Sr (Brown et al., 2003). In studies of the intensity of weathering of sediment in large river systems draining areas representative average continental crust, (Gaillardet et al., 1999; 2004) used weathering indices defined by pairs of elemental which have similar characteristics relative to the degree of differentiation between the upper crust and primitive mantle abundances but exhibit significant differences in the weathering environment. An example of such a weathering index is

\[
I_w = \frac{\frac{Sm}{Na}_{sed}}{\frac{Sm}{Na}_{crust}}
\]

(Gaillardet et al., 1999) showed that for sediments in the world rivers Na weathering was always greater than unity (\(I_w = 1 \text{ to } 25\)) indicating depletion relative to the continental crust.

5.04.3.1.2 Mass Transfer

While weathering indices are useful in characterizing relative weathering intensities, they do not define the amount of a specific component mobilized during weathering, a prerequisite to calculating quantitative weathering rates (\(\Delta M\) in Equation 1). A more rigorous approach is the use of mass transfer coefficients which defines absolute mass losses. Such losses require comparing the concentration of a weatherable component \(j\) in a soil or regolith \(C_{j,w}\) against its corresponding concentration in the rock or protolith \(C_{j,p}\). This component can consist of an element, isotope or mineral. The concentration of \(C_{j,w}\) reflects not only its own mass changes but also relative changes due to gains and losses of other components in the regolith, as well as external factors such as compaction or dilation of the soil or regolith. The most common
method for overcoming such effects is to compare the ratio of the mobile component $j$ to the ratio of an additional component $i$, which is chemically inert during weathering (Merrill, 1906; Barth, 1961).

Brimhall and Dietrich (1987) defined the concentration ratio of a weatherable component in the regolith and protolith based on the relationship

$$
\frac{C_{j,w}}{C_{j,p}} = \frac{\rho_p}{\rho_w} \left( \frac{l}{\varepsilon_j + 1} \right) (1 + \tau_j) \tag{7}
$$

in which the change in the mobile element concentration ratio $C_{j,w}/C_{j,p}$, resulting from weathering, is dependent on 3 parameters: (1) the ratio of the bulk densities of the parent and weathered material, $\rho_p/\rho_w$, (2) the volume change resulting from soil compaction or extension described by the strain factor $1/\varepsilon_j + 1$ where $\varepsilon_j = V_w/V_p - 1$ and (3) the mass transport coefficient $\tau_j$. The strain and volume changes describe closed system contributions which occur without mobilization of the component under consideration (i.e., $C_j$). The term $\tau_j$ describes the mobility of component $j$ within a unit volume of regolith.

The volumetric strain or volume change is calculated from the ratios of densities and concentrations of the inert element $i$ in regolith and protolith

$$
\varepsilon_i = \frac{\rho_p C_{i,w}}{\rho_w C_{i,p}} - 1 \tag{8}
$$

Positive values of $\varepsilon_i$ indicate regolith expansion and negative values indicate regolith collapse. A value of $\varepsilon_i \approx 0$ is indicative of isovolumetric weathering.

The mass transfer $\tau_j$ in Equation 7 is such that (Brimhall and Dietrich, 1987)

$$
\tau_j = \frac{C_{j,w}}{C_{j,p}} \frac{C_{i,p}}{C_{i,w}} - 1 \tag{9}
$$

When $\tau_j = 0$, no mobilization of the weatherable component $j$ has occurred. When $\tau_j = -1$, complete mobilization has occurred. An external addition of component $j$ has occurred if $\tau_j > 0$. Calculations of strain $\varepsilon_j$ (Equation 8) and mass transfer $\tau_j$ (Equation 9) require that at least one component in the regolith ($C_j$) remains inert or immobile during chemical weathering.
Commonly assumed conservative elements include Zr (Harden, 1987), Ti (Johnsson et al., 1993) Nb (Brimhall and Dietrich, 1987), or some rare earth elements. However there is considerable disagreement in the literature as to the relative motilities of these elements under differing weathering conditions (Gardner, 1980; Hodson, 2002). As proposed by White (1995), probably the best approach to establishing conservation is to compare the relative mobility of a suite of refractory elements for a specific weathering environment.

The composition of the parent material or protolith, $C_{j,p}$ is also required in calculating the above weathering parameters (Equations 7 - 9). This composition is generally easy to determine for regoliths developed in situ on relatively homogenous bedrock. Determinations of parent concentrations are more difficult for heterogeneous protoliths such as some sediments. One approach is to equate the parent material to similar recent unweathered sediments, assuming that the depositional environment has not changed significantly. An example is the weathering of beach sands in marine soil chronosequences (Chadwick et al., 1990). The second approach utilizes the common observation that weathering intensity decreases with depth in a regolith (see weathering indices in Figure. 4). Samples acquired at sufficient depths may therefore reflect the unweathered protolith composition (see example of White et al., 2007).

A simple graphical method for representing mass transfer and volumetric changes in a regolith is to plot $e_j$ (Equation 8) versus $\tau_j$ (Equation 9), producing graphs with quadrants representing 4 distinct weathering conditions (Figure 5). Values of $e_j < 1$ indicate collapse, while values of $e_j > 1$ indicate volume increases or dilation. Similarly, $\tau_j < 1$ denotes mass loss ($\Delta M_j < 0$) and $\tau_j > 1$ indicates addition of mass ($\Delta M_j > 0$). This approach is illustrated in Figure 5 which contains Si, Ca, Al and Fe distributions in three regolith profiles of varying age from the Santa Cruz chronosequence in California (White et al. 2008, 2009). Here quartz is employed as the immobile component in Equations 8 and 9, with the deepest sample in each profile is used as the protolith. Positive values of $e_j$ generally correspond to shallow soils that are dilated due to bioturbation, addition of organics, and inputs of eolian material. In contrast, regolith from greater depths indicate collapse as a result of chemical weathering (values of $e_j$ are negative).
The mass transfer coefficient $\tau_j$ expresses element mobility during weathering relative to the protolith composition. Si in Figure 5a is essentially immobile ($\tau_{Si} \approx 0$) because it is primarily contained in quartz, which is assumed to be inert during weathering (White et al. 2008). Negative values of $\tau_{Si}$ are therefore related to loss of Si from minerals other than quartz. In contrast, Ca in Figure 5b is significantly depleted due to plagioclase weathering in both the collapsed and dilated soils, and is also strongly correlated with the age of the soil in the chronosequence. Values of $\tau_{Ca} \approx -1$ indicate near-complete depletion of Ca throughout much of the oldest terrace (226 ka) while $\tau_{Si} \approx 0$ indicates that Si remains unreactive or immobile in most of the deeper parts of the younger terrace (90 ka).

As commonly seen in many regoliths, Al and Fe are mobilized in the Santa Cruz soils during dissolution of primary silicate minerals but are subsequently incorporated into secondary clays and oxide minerals. In Figures 5c and d, these elements appear depleted ($\tau_j < 1$) in zones of collapse that correspond to deep weathering in the older terraces. In contrast, Al and Fe are concentrated ($\tau_j > 1$) in zones of dilation that are associated with relatively shallow soils containing a clay and Fe oxide argillic horizon that accumulates as the terraces age. These patterns for Al and Fe signify either external inputs at the surface (e.g., from dust) or mobilization by weathering at depth and re-precipitation in shallower soils via biological uptake (bio-lifting).

The applicability of the above approach (Equations 8 and 9) in describing elemental mobilities in soil profiles is shown in Figure 6 for a 350 kyr old regolith at Panola, Georgia USA (White et al., 2000; 2001). This profile consists of a dense unstructured kaolinitic soil, overlying a porous saprolite resting on granodiorite bedrock. Saprolites, common in many subtropical to tropical weathering environments, are clay-rich regoliths that retain the original bedrock texture. Volume changes in the deep Panola saprolite and bedrock, calculated from Zr, Ti, and Nb concentrations, center close to zero, i.e. $\epsilon = 0$ (Equation 8), indicating that weathering is isovolumetric (Figure 6a). In contrast, the shallowest soils have undergone volume increases due to bioturbation and the introduction of organic matter.

Figure 6 Near Here.
Values for $\tau_j$ for Al, F and Mg (Equation 9) cluster near zero in the Panola bedrock below 10.5 m indicating no elemental mobility (Figure 6b). Ca and Na are almost completely mobilized at depths of between 9.5 and 4.5 m where Si is moderately depleted. Bedrock weathering is highly selective, with other elements remaining essentially immobile ($\tau_j = 0$). K and Mg are mobilized in the overlying saprolite and Fe and Al are strongly depleted in the upper soil and enriched in the lower soil horizons, which is indicative of downward Fe and Al mobilization and subsequent re-precipitation.

The total elemental mass loss or gain occurring in the Panola regolith ($\Delta M$) is determined by integrating the mass transfer coefficient $\tau_j$ over the regolith depth $z$ (m) and unit surface area (1 m²) such that (Chadwick et al., 1990; White et al., 1996)

$$\Delta M_{j,\text{solid}} = \rho_p \frac{C_{j,p}}{m_j} \int_0^z (\tau_j) dz$$  \hspace{1cm} (10)

where $m_j$ is the atomic weight of element $j$. The elemental losses in each horizon of the Panola profile are calculated from Equation 10 and tabulated in Table 2.

**Table 2 Near Here**

Element mobility in the Panola regolith can be converted to changes in primary and secondary mineral abundances (Figure 7) using a series of linear equations describing mineral stoichiometries (Bricker et al., 2004). Table 2 indicates that initial bedrock weathering removes 95% of the plagioclase. K-feldspar weathering predominates within the overlying saprolite and biotite weathering occurs both in the saprolite and shallower soil. Secondary kaolinite is produced within the bedrock from plagioclase weathering and in the saprolite and deeper soils from K-feldspar and biotite weathering. The loss of kaolinite in the shallowest soils implies either dissolution or physical translocation to deeper soil horizons. Fe-oxides are formed by oxidation of Fe released from biotite weathering in the saprolite. As in the case for kaolinite, Fe-oxides decrease in the shallow soils.

**Figure 7 Near Here.**

**5.04.3.1.3 Profile categories**
Mass transfer data can be most easily interpreted for weathering profiles developed on topographically flat landscapes with minimum erosion or sediment accretion. For such systems, three basic profile categories can be discerned (Brantley et al., 2008): i) immobile profiles, which contain parent concentrations of a given component ($\tau_j = 0$) at all depths; ii) depletion profiles, showing depletion of the element of interest with respect to the immobile element ($\tau_j < 0$); and iii) addition profiles exhibiting enrichment of the mobile element with respect to the immobile element ($\tau_j > 1$).

Figure 8 shows soil profiles from central Pennsylvania, USA developed on the organic-poor, Silurian Rose Hill shale in the Susquehanna Shale Hills Critical Zone Observatory (SSHO) (Brantley and White, 2009). The site is a tectonically quiescent, forested, first-order catchment with gentle slopes dissected by an ephemeral stream (Jin et al., 2010). In Figure 8a, $\tau_i = 0$ for both Nb and Zr throughout the profile indicating that those elements are neither added nor lost from the soil relative to Ti, the assumed immobile element ($i = Ti$ in Equations 6 and 7). Thus, Ti, Nb, or Zr could have been used as the immobile element in Equations 8 and 9 for that soil. It should be noted that this is not true for all profiles as the relative mobility of such conservative elements varies with the mineralogy of the protolith and weathering conditions (Gardner 1980; Kurtz et al. 2000; Hodson 2002). However, in Figure 8a, the agreement among Ti, Zr, and Nb (i.e., $\tau_j \approx 0$) is consistent with the conservation of these elements during weathering of the Rose Hill shale.

In contrast to the immobile profiles shown in Figure 8a, Figure 8b shows a depletion profile reflecting the loss of Cu during weathering of the Rose Hill shale. Depletion profiles for a given element or mineral phase can be categorized as partially developed profiles (i.e., partially depleted at the surface: $-1 < \tau_j < 0$ as shown in Figure 8b) or fully developed profiles (i.e., completely depleted at the surface: $\tau_j = -1$). These classifications provide insight into soil development processes. For example, depletion of Mg in the Rose Hill regolith profile was interpreted to reflect the dissolution of clays near the soil surface (Jin et al., 2010).

External inputs of elements to regolith create addition profiles, which exhibit net addition of an element relative to an immobile element ($\tau_j > 0$ in Equation 9). Such profiles typically
indicate atmospheric deposition (e.g., Mn in Figure 8d), or biological fixation (e.g., C in Figure 8d). Addition profiles generally are the result of inputs at the surface and subsequent redistribution downward by leaching or bioturbation. Thus, addition profiles are typified by concentrations that are highest at the surface, decreasing to protolith concentration at depth.

These three profile categories are end members and profiles can occur that exhibit characteristics of more than one category. The most common of these is termed a depletion – enrichment profile, which describes the case of an element that is leached at the surface and reprecipitates at depth in the regolith. An example of a depletion-enrichment profile is the E-Bs, E-Bt sequence commonly observed in forest soils where Al is mobilized by organic ligands near the surface and reprecipitated at depth, where concentrations of organic ligands are lower. Similarly, Fe often exhibits depletion-enrichment profiles, as do other elements that have affinity for Fe or Al (e.g., P). An element defining a depletion-enrichment profile may be conservative, $\Delta M = 0$, depleted, $\Delta M < 0$, or added, $\Delta M > 0$.

Depth profiles of nutrient elements commonly exhibit characteristics primarily developed by biological processes and thus are termed biogenic profiles. These profiles commonly exhibit trends that are opposite to depletion-enrichment profiles. These profiles typically describe the release of biological nutrients such as K or Ca from the parent material followed by redistribution by bio-lifting (Figure 8e). Therefore, biogenic profiles generally show depletion at depth and enrichment at the surface. Plant roots and fungal hyphae bio-lift nutrients by secreting organic acids that contribute to mineral dissolution at depth and then taking up the nutrients into their biomass and recycling them near the surface.

Some profiles, particularly for nutrient elements, are not easily categorized. For example, primary P is usually derived from the mineral apatite and can produce a depletion profile if net loss of P occurs. However, P is an essential, often limiting, nutrient and as such it frequently exhibits characteristics of biogenic profiles. Moreover, when P is released from apatite or during decomposition of biomass, it frequently sorbs onto Fe oxyhydroxides. These processes can impose a depletion-enrichment character on to P profiles, which can overprint the biogenic character, producing very complex P profiles in some regoliths.
5.04.3.1.4 Time evolution of profiles

The previous section did not consider how the various types of concentration-depth profiles evolved with time. Where erosion is insignificant, for example in a stable alluvial terrace, a depletion profile such as that shown in Figure 8b moves downward with time at the regolith advance or weathering advance rate. This is indicated by the solid state weathering velocity \( w \) in Figure 3b. The development of a solid state profile with time is shown in Figure 9 for a model system consisting of albite in a quartz matrix experiencing no erosion (Lebedeva et al., 2007). Individual profiles are plotted as snapshots in time as they move downward. The uppermost two profiles are partially developed (or partial depletion) profiles in which the upper boundary, i.e. the surface, still contains the weatherable mineral phase \( \tau_j > -1 \). The lower profiles demonstrate fully developed (or completely depleted) profiles defined by an upper surface where \( \tau_j = -1 \) and a lower boundary, i.e., the protolith where \( \tau_j = 0 \). The schematic in Fig. 3b is representative of a fully developed soil profile. Once the profile becomes completely depleted with respect to albite at the surface, the geometry of the profile stays constant while moving downward. At this point the profile is quasi-stationary (Lichtner, 1988). The profile retains its geometry but moves downward at the weathering advance rate \( \omega \).

For depletion profiles such as shown in Figure 9, two important parameters are fitted by the model, the maximum depth from the surface to the reaction front, and the thickness of the reaction front. In turn, these parameters are related to the weathering (regolith) advance rate and the mineral reaction rate (Figure 3). For a non-eroding profile, the depth of the weathering front increases with time. Initially the reaction front also thickens (the depth interval over which a given component is depleted within a profile) but becomes constant in time for once the quasi-stationary profiles have developed.

Analytical models utilizing parameters for flow and rate constants for dissolution have been derived to treat depletion profiles when only a single component reacting within a single phase system (Lichtner, 1988). In such models, the thickness of the reaction front is related to the ratio of the rates of transport to dissolution. For example, for diffusion-limited weathering rind formation in low porosity rock where transport is dominantly by diffusion, the thickness of
the reaction front ($h$) represents a balance between the product of the porosity ($\phi$) and effective diffusivity ($D$) divided by the product of the rate constant for solubilization of a given element ($k$) and the mineral-water interfacial area ($A$) (Lichtner, 1988):

$$h = \left( \frac{\phi D}{k A} \right)^{\frac{1}{2}}.$$  

(11)

In contrast, for a reaction front developed on a higher permeability matrix such that advection ($v$) dominates the reaction front thickness $h$ can be expressed (Lichtner, 1988):

$$h = \frac{v}{kA}$$  

(12)

Multiphase multicomponent chemical systems incorporate species that are coupled between reacting phases and thus cannot generally be described analytically without simplifying assumptions (Lebaeva et al., 2007). For example, many analytical models for soils either explicitly or implicitly rely on the assumption that the reacting mineral, e.g., albite, is dissolving within a largely nonreactive matrix (Figure 9). For such a treatment, the rate constant fit to the data is an operational rate constant that may or may not be comparable to laboratory measurements where dissolution was measured without the presence of other phases. This is presumably one of the reasons that rate constants from field observations do not match those from laboratory observations.

5.04.3.1.5 Utilization of Soil Chronosequences

A particularly valuable approach to investigating the effect of time on evolution of soil weathering profiles has been the use of soil chronosequences, which are defined as a group of soils that differ in age and, therefore, in duration of weathering. These soils have similar parent materials and have formed under similar climatic and geomorphic conditions (Jenny, 1941). Individual profiles in a chronosequence, therefore, provide “snap shots” of the progressive nature of chemical weathering with time allowing comparison of critical zone processes and weathering fluxes over both geologic and contemporary time scales.
Chronosequences include marine and alluvial sediment deposits and lava flows. Studies of chronosequences (e.g., Bockheim, 1980; Birkland, 1984; 1990; Harden, 1987; Jacobson et al., 2002) have quantified systematic changes in weathering properties of soils with ages ranging from 1 to 4000 kyrs. Mass balance studies have characterized mineralogical changes (Mokma et al., 1973; Mahaney and Halvorson, 1986), chemical changes (Brimhall and Dietrich, 1987; Merritts et al., 1992; White et al., 1996; 2008) and development of etch pitting (Hall and Horn, 1993) as functions of soil age. An important conclusion of these chronosequence studies is that the rates of primary silicate weathering generally decrease with duration of weathering.

One well studied example is the Santa Cruz chronosequence, which is comprised of 5 marine terraces (SCT 1-5, from youngest to oldest) near the city of Santa Cruz, California, adjacent to the Pacific Ocean, and approximately 50 km SW of San Francisco. These 5 terraces document how the original protolith evolved over 226 kyrs of weathering. The original sedimentary deposit was comprised principally of reworked granitic beach sediments deposited on a succession of wave cut terraces which were subject to gradual tectonic uplift. Weathering profiles showing the residual plagioclase in progressively older soils, normalized to the amount contained in the original protolith, are shown in Figure 10 (White et al., 2008). The youngest two soils are examples of incompletely developed profiles in which significant amounts of residual plagioclase remain in the shallow soils. The oldest three soils, representing more than 100 kyrs of weathering, are fully developed weathering profiles with small residual amounts of plagioclase near the soil surface accounted for by bioturbation and dust inputs.

Figure 10 Near Here

Residual plagioclase distributions exhibits approximate linear increases at intermediate soil depths which correspond to the weathering or reaction fronts described in Figure 3b. A more detailed plagioclase distribution for the SCT 4 terrace is shown Figure 11 in which residual plagioclase is plotted in terms of volume concentration where $\Delta M_j$ is the difference between the regolith and protolith concentrations. Dividing $\Delta M_{total}$ by the depth interval over which this loss occurs ($z = 5$ m in Figure 11) results in a linear weathering gradient $b$, of 2.1 m$^4$ moles$^{-1}$ (White et al., 2008). The mineral weathering rate in Equation 4 is also directly proportional to the weathering velocity $w$. For the Santa Cruz, cosmogenic $^{10}$Be data indicate that very little erosion...
has occurred on the relatively flat terrace surfaces (Perg et al, 2001). Under such conditions, the
profile progressively thickens as weathering progresses deeper into the beach sand protolith at a
constant rate $\omega$, defined by the depth and age of the weathering profile. The change in profile
depth with time is shown at other times by the dashed lines in Figure 11.

**Figure 11 Near Here.**

A fuller characterization of the weathering profiles shown in the schematic in Figure 3 as
well as for the Santa Cruz soils in Figure 10, must also account for the nonlinearity of solid state
weathering profiles, in particular the asymptotic characteristics when regolith compositions
become significantly depleted near the soil surface as well as when they approach protolith
compositions at depth. The solid curves, which reproduce the residual plagioclase distribution in
the Santa Cruz terraces, were calculated using a spreadsheet model (a *profile calculator*; White
et al., 2008). The model calculates the plagioclase profiles by using the best-fit values for the
fluid fluxes $q_h$ and kinetic rate constants $k_{plag}$ and incorporating an exponential surface area term
and a thermodynamic saturation effect, both of which are primarily responsible of the asymptotic
characteristics of the profiles (White et al, 2008). Additional approaches for fitting non-linearity
in weathering profiles, including analytical solutions and coupled mass transport models are
reviewed by Brantley and White (2009).

The profile calculator was also used extrapolate soil profiles forward and backward in
time, given present weathering conditions. For example, the dashed lines for SCT 1 in Figure 10
represent a sequential forward extrapolation in time to the ages of the SCT 2 through SCT 5
profiles using the present day SCT 1 weathering parameters. Conversely, the SCT 5 plot contains
profiles that are extrapolated backward in time to the ages of SCT 4 through SCT 1 profiles
using present day weathering SCT 5 parameters. If current weathering conditions remained
identical for each of the five terraces, the profile geometry and the total amount of plagioclase
weathered should be identical after 226 kyrs. of weathering. Overall chronosequence
development, represented by the shaded areas in Figure 10 is generally similar when using the
SCT 2, SCT 3, SCT 4 and SCT 5 profiles as the baselines. Clearly the greatest discrepancy
occurs in the forward extrapolations in time of the SCT 1 terrace. These results predict a much
less intensively weathered terrace sequence than that which exists today. This discrepancy results
primarily because the fitted fluid flux \( q_h \), the principal parameter controlling weathering, is significantly lower for SCT 1 than for the other terraces.

### 5.04.3.1.6. Steady State Denudation and Weathering Profile Development

Physical denudation, here referred to as erosion, is commonly estimated from rates of sediment transport or by cosmogenic nuclide distributions (Granger and Riebe, this volume). If the rate of erosion, \( E \) (m s\(^{-1}\)), equals the rate of weathering advance, \( \omega \) (m s\(^{-1}\)), the profile is said to be in steady-state, in which case the profile geometry and thickness remains constant with time. Unlike the zero erosion case, steady state can occur regardless of whether the profile is fully developed or not.

Riebe et al. (2003) characterized chemical and physical denudation associated with steady state weathering of regoliths by the relationship.

\[
D \cdot C_{j,p} = E \cdot C_{j,w} + W
\]

where the denudation rate \( D \) (m s\(^{-1}\)) of a mobile component \( j \) equals the sum of \( j \) derived from physical erosion \( E \) (m s\(^{-1}\)) and the chemical weathering flux \( W \) (m s\(^{-1}\)). This relationship is valid under the assumption that the regolith is maintained at a constant thickness and is not a sink for component \( j \).

In the case of a conservative component \( C_i \) that is not mobilized during weathering (e.g., Zr):

\[
D \cdot C_{i,p} = E \cdot C_{i,w}
\]

is expressed as a fraction of the total denudation. Substituting Equation 14 into 13 defines the chemical flux for an individual mobile component \( j \)

\[
W = D \left[ C_{j,p} - C_{j,w} \frac{C_{j,p}}{C_{j,w}} \right]
\]

The weathering flux \( W \) can be expressed in a non-dimensional form by normalizing by the total denudation rate for component \( j \):
where the parameters in parenthesis is defined as the chemical depletion factor or CDF (Riebe et al. (2003), which is equivalent to negative $\tau_j$ (Equation 9).

In reality, many regoliths are either aggrading or degrading, but eventually reach steady state, as illustrated in Figure 9 (e.g., Fletcher et al., 2006; Hren et al., 2007; Dosseto et al., 2008). In a steady-state eroding profile, a given volume, or layer, of solid material can be conceptualized as moving upward across the weathering front. Therefore, the thickness of any given layer in a steady-state weathering profile and the rate of transformation of each layer into the overlying (more weathered) layer must be constant in time (Figure 9).

In a non-eroding system, partially-developed profiles ($-1 < \tau_j < 0$ at the surface) are transient phenomena, eventually evolving into fully-developed profiles. However under constant erosion, partially-developed profiles can represent true steady-state conditions. Such a profile is shown in Figure 12 for relatively fast erosion rates ($E > 0.0075$ m ky$^{-1}$) in an idealized, diffusion-limited (low-porosity) system containing only albite and quartz weathering to kaolinite (Lebedeva et al., 2009). Alternately, if erosion rates become slower, a steady-state profile could develop into a fully developed profile ($E < 0.0075$ m ky$^{-1}$, Figure 12). Thus, considering rates of erosion together with weathering rates affects the steady state geometry of weathering profiles.

As mentioned previously, for steady-state weathering systems as depicted in Figure 12, the linear rate of erosion equals the weathering advance rate. At the high erosion rate ($E$) end member, profiles are *incompletely developed* (e.g., $E > 0.0075$ m ky$^{-1}$ in Figure 12) and the chemical weathering fluxes of Na and Si approach a linear function of the albite dissolution rate constant. In contrast, in systems with thin, fully developed reaction fronts (e.g., $E < 0.001$ m ky$^{-1}$ in Figure 12) the chemical weathering flux is *not* a direct linear function of the dissolution rate constant.

**Figure 12 Near Here.**

When $E$ is small compared to the albite weathering rate constant, $k$, a very sharp reaction front is observed; in contrast, when $E$ is fast compared to $k$, a steep and thicker reaction front is
observed (Figure 12). These reaction front characteristics are indicative of different steady-state weathering regimes. A sharp reaction front within a completely depleted profile is characteristic of the local equilibrium regime, $E < 0.001$, while a partially depleted profile is characteristic of the kinetic regime, $E > 0.0075$ (Lebedeva et al., 2007; 2009). Between these two end members, profiles may show complete depletion at the land surface but also show relatively wide reaction fronts resulting in the transition regime, wherein chemical weathering fluxes vary with both dissolution and erosion rate ($0.001 < E < 0.0075$). These regimes can be compared to the transport-limited (similar to local equilibrium) and the weathering-limited regimes (similar to kinetic regime) hypothesized for catchments (see section 5.04.7.5.1 Transport vs. chemical weathering regimes). Simulated steady-state weathering profiles for model “rocks” containing albite + quartz + kaolinite are shown in Figure 12, demonstrating the relationship between erosion rate, $E$, and weathering regime.

The chemical flux in these diffusion-limited models (Figure 12) is a function of the solute concentration gradient at the surface. While this gradient is relatively insensitive to variations in $E$ in the kinetic regime, it varies significantly as a function of $E$ in the transition and local equilibrium regimes. Therefore, these models demonstrate that chemical fluxes are sensitive to the erosion rate in the transition and local equilibrium regimes (lower $E$), but not in the kinetic regime (high $E$). In contrast to the profiles shown in Figure 12, which assume transport by diffusion only, similar models for advective transport result in thicker reaction fronts (Lebedeva et al. 2009).

### 5.04.3.2 Changes Based on Solute Compositions

The alternative method for calculating weathering rates is based on the mass of solutes produced during weathering ($\Delta M$ in Equation 1). This approach commonly involves comparing changes between initial and final solute concentrations $\Delta c_j$ (molar) in a known volume of water $V_s$ (L) such that

$$\Delta M_{j,\text{solute}} = \Delta c_j V_s.$$  

(17).

The above equation is analogous to Equation 10, which describes mass changes in the solid state.
5.04.3.2.1 Characterization of fluid transport

Water is the medium in which weathering reactants and products are transported to and from the minerals undergoing reaction. In addition, as suggested in Figure 3a, the flux density of water $q_h$ (m s$^{-1}$) is critical in controlling the development of solute profiles as well as controlling fluid residence times in soils and aquifers. Clearly, a detailed discussion of hydrologic principles is beyond the scope of this chapter, but several aspects critical to understanding natural weathering will be briefly mentioned.

In the case of diffusive transport, bulk water is immobile and movement of solutes occurs by Brownian motion. Under such conditions, the flux $Q$ of a solute reactant or product is determined by the product of the diffusion coefficient $D$ (m$^2$s$^{-1}$) and the concentration gradient as given by Fick’s First Law (Allen and Cherry, 1979)

$$Q_j = -D_j \frac{\partial c_j}{\partial z}$$

The diffusion coefficients of solutes are commonly on the order of $10^{-9}$ m$^2$s$^{-1}$ making diffusive transport effective only at or near the mineral surface. On a nanometer-scale, solutes diffuse along and across water layers structurally influenced by the silicate surface. Microscopic diffusion occurs through stagnant water contained within internal pore spaces and etch pits or along grain boundaries.

More commonly, solutes move through the weathering environment along with the advective flow of water. In this case, the solute flux is the product of the solute concentration and the flux density of water $q_h$, i.e.,

$$Q_j = c_j q_h$$

where $q_h$ (m s$^{-1}$) is defined as the product of the hydraulic conductivity $K_m$ (m s$^{-1}$), and the hydraulic gradient $\nabla H$ (m m$^{-1}$) (Hillel, 1982)

$$q_h = -K_m \nabla H$$
The above relationships (Equation 18 to 20) define the basic processes by which solutes are transported during chemical weathering. As indicated in Figure 3a, the hydraulic flux \( q_h \) also serves as the primary control on solute weathering profiles. For unsaturated flow, which dominates in most soil and shallow regolith environments, both \( K_m \) and \( \nabla H \) are dependent on variations in water content. The change in head with depth can be described such that (Hillel, 1982)

\[
\frac{dH}{dz} = \frac{dh_g}{dz} + \frac{dh_p}{dz}
\]

where \( h_g \) is the gravitational head at any point and \( h_p \) is the head related to the matric potential of the soil mineral surfaces. Determinations of fluid, and conversely chemical fluxes based on Equations 20 and 21 are difficult for most unsaturated conditions due to the non-linear dependence of conductivity and head potentials on moisture content. Special cases for Equations 20 and 21 are discussed by Stonestrom et al. (1998) in which constant matric potentials or tensions exist within a vertical section of a weathering regolith (i.e \( dh_p/dz = 0 \)).

An example of the extreme variability in hydraulic conductivity and thus solute transport that commonly occurs with changes in moisture content is shown in Figure 13a for the Riverbank soil, which is part of the Merced chronosequence situated in Central California (White et al., 2005). Seasonal pore water saturation in the shallow soils, on a yearly basis varies between minimally saturated to fully saturated soils, a wide range typical of soils influenced by a relatively dry Mediterranean climate.

Figure 13 Near Here.

The corresponding experimental hydraulic conductivities (\( K_m \) in Equation 20) for samples of the Riverbank soil, shown in Figure 13b, exhibit even larger variabilities (Stonestrom et al., 1998). In general the lowest conductivities occur at about one meter depth in the soil which corresponds to maximum clay contents in an argillic horizon (Figure. 13b). In sandier sediments, above and below this horizon, conductivities (Equation 20) are much higher close to hydrologic saturation but approach lower clay conductivities as saturation declines to less than 60%. Much drier soil conditions throughout most of the year (Figure 13a) result in unsaturated conductivities that are far below what can be measured experimentally. The end result is that solute movement
under hydrologically unsaturated conditions is commonly not continuous, as assumed in most weathering scenarios, but is episodic, responding to specific recharge events such as major storm events or seasonal snow melt. At most times, pore waters remain stagnant, a condition reflected in the approach to thermodynamic saturation of many pore waters.

5.04.3.2.2 Weathering based on solutes in soils

Solute profiles reflect contemporary weathering rates integrated over the residence time of water in the regolith or aquifer, commonly on time scale of years to decades. The calculation of weathering rates from solute profiles (Figure 3a) is analogous to the calculation of weathering rates from solid profiles (Figure 3b). The solute weathering rate is expressed as the change in solute composition as a function of the rate of water movement through the pore spaces in the regolith. Such calculations are complicated by the fact that individual solute species are commonly produced by more than one weathering reaction. For example, in granite weathering, aqueous silicon is produced during dissolution of plagioclase, K-feldspar, biotite, hornblende, and quartz. In addition, precipitation of secondary minerals, such as kaolinite, removes aqueous silicon from solution (Equation 2). Therefore, solute weathering rate calculations require detailed information on mineral abundances and stoichiometries in the regolith and protolith.

An example of the use of solute distributions to calculate weathering rates is shown in Figure 14 for a deep weathering profile from the Rio Icacos watershed in the tropical Luquillo Mountains of Puerto Rico (White et al., 1998). The upper 0.5 m of this regolith is dense kaolinitic clay overlying nearly 10 m of saprolite resting on quartz diorite bedrock consisting predominately of quartz, plagioclase, hornblende and biotite. As indicated in Figure 14, significant variations in solute K, Mg and Si occur in the upper clay zone due to the effects of evapotranspiration and biological cycling of mineral nutrients. At greater depths (> 2 m), this variability is damped with solute species exhibiting consistent increases with depth. Such distributions represent solute weathering gradients (Figure 3a) reflecting both the rate at which solute reaction products are contributed from chemical weathering and the rate of pore water movement through the soil.

Figure 14 Near Here

33
Based on the solute and hydrologic information outlined above, Murphy et al (1998) derived a rate equation for biotite weathering in the Luquillo regolith

\[
R_{\text{biotite}} = \frac{q_h}{\beta V_{\text{biotite}} \rho (1-\phi) S} \frac{dc}{dz}
\]

in which the weathering rate is the product of the water flux density \(q_h\) (Equation 19) and the solute gradient describing the linear change in solute Mg or K with depth in the regolith \(dc/dz\). \(V_{\text{biotite}}\) is the volume fraction of biotite in the regolith, \(\beta\) is the stoichiometric coefficient describing the Mg and K content of the biotite. \(\rho, \phi\) and \(S\) are the respective density, porosity and BET surface area terms. The resulting biotite weathering rate in the Luquillo regolith, based on Mg and K pore water solute distributions, is reported in Table 4.

In addition to mineral distributions measured in soils of the Santa Cruz chronosequence (Figure 10), solute distributions in unsaturated pore waters were also measured over a several year period using nested suction water samplers (White et al., 2009). With the exception of higher concentrations in the shallowest soils, reflecting effects of evapotranspiration, pore water Si and Na increase with increasing depth throughout the terrace deposits (Figure 15a and b). The primary weathering source of these solutes is plagioclase as indicated by the correlation with its solid state weathering profile (Figure 10). Below the interface in the underlying Miocene sandstone, Na and Si compositions become constant with depth suggesting reduced permeability and thermodynamic plagioclase saturation.

**Figure 15 Near Here**

Parameters shown in Figure 15c are essentially equivalent to those shown in the original schematic in Figure 3a. Solute distributions are first converted to volume concentrations, analogous to solid state mineral distributions (Figure 10). \(b_{\text{solute}}\), is calculated by a least square fit to the linear pore water distributions with depth. The weathering velocity is equivalent to the hydraulic flux estimated based on an independent hydrologic balance. Assuming constant hydrologic conditions the position of the solute weathering gradient will not change over the pore water residence time.
The corresponding weathering rate is calculated based on Equation 3 (White et al., 2009) and listed in Table 4.

5.04.3.2.3 Weathering based on solutes in groundwater

Several characteristics distinguish chemical weathering in aquifers from soils. Groundwater weathering occurs under hydrological saturated conditions in which fluid flow is governed by Darcy’s law and is proportional to the product of the saturated hydraulic conductivity and the gravitational gradient (Equation 20). Groundwater movement commonly occurs as matrix flow through unconsolidated sediments or as fracture flow in bedrock. The saturated hydraulic conductivities are dependent on porosity, tortuosity and other factors intrinsic to the geologic material and vary over a wide range from $10^{-4}$ m s$^{-1}$ for clean sand to $10^{-12}$ m s$^{-1}$ for crystalline rocks (Allen and Cherry, 1979).

The physical isolation of ground water aquifers relative to that of soils is advantageous for characterizing weathering rates because biologic and short term climatic perturbations are diminished. However, because of greater physical isolation, the characterization of mineral distributions, aquifer heterogeneities and mineral surface areas becomes more difficult. The earliest and simplest characterization of chemical weathering in groundwater was based on spring or seep discharge (Garrels and Mackenzie, 1967). In such cases, the changes in solute concentration due to weathering are assumed to be the difference between the discharge compositions and atmospheric contributions in precipitation. The fluid flux is the measured spring or seep discharge. The disadvantage of such an approach is that no direct information on the spatial extent of the weathering environment is known, making normalization of the weathering rate to surface area difficult. Several recent approaches are advanced in estimating the spatial extent of spring discharge and corresponding magnitude of chemical weathering (Manga, 2001; Pacheco and Van der Weijden, 2002).

A more rigorous and intrusive approach to groundwater weathering is to characterize changes in solute concentrations measured in an array of wells in an aquifer (e.g., Zhu, 2005; Kenoyer and Bowser, 1992). Determination of chemical weathering rates based on this approach
requires that changes in solute concentrations occur along defined flow paths and that the rate of groundwater flow is known. This approach is commonly referred to as an inverse problem in which weathering reactions are computationally fitted to account for the observed chemical changes in the groundwater (Parkhurst and Plummer, 1993). Such studies tie the rates of chemical weathering closely to a detailed understanding of fluid flow in an aquifer, which is commonly described by groundwater flow models.

The above approach is illustrated in the determination of chemical weathering rates in ground waters in glacial sediments in northern Wisconsin, USA (Kenoyer and Bowser, 1992; Bullen et al., 1996). The flow path is defined by subaerial recharge from Crystal Lake moving downgradient across a narrow isthmus and discharging into Big Muskellunge Lake (cross sections in Figure 16). Water levels and in situ slug tests, measured in an array of piezometers, determined the hydraulic conductivities and gradients plotted in Figure 16a and 16b. Groundwater velocities were determined by application of Darcy’s law to these measurements and were checked using tracer tests. The resulting fluid residences in groundwater at various positions in the aquifer were then calculated based on the distance along the flow path (Figure 16c).

Figure 16 Near Here

Groundwater solutes, sampled from the piezometers, exhibited significant trends as shown by Si and Ca distributions plotted in Figure 17. The core of the groundwater at the upgradient end of the cross section is recharged directly from Crystal Lake. Significant changes in the chemistry of this plume take place along the flow path due to the dissolution of well-characterized silicate minerals that compose the aquifer. Various proportions of minerals phases were computationally dissolved using the PHREEQE code (Parkhurst and Plummer, 1993) until the best fit to the solute trends along the flow path was obtained. The resulting mineral masses were then divided by the fluid residence time and estimates of mineral surface area to produce the plagioclase and biotite weathering rates tabulated in Table 4.

Figure 17 Near Here

5.04.3.2.4 Weathering based on surface water solutes.
Approaches describing weathering in surface waters in catchments and rivers are reviewed by Galliand (this volume) and Viers (this volume) and are only briefly considered here. As in the case of soils and aquifers, the determination of such rates in watersheds is closely associated with an understanding of the hydrology. Commonly, solute compositions and fluid fluxes are determined at a gauged position on a stream or river. Fluid flow, expressed in terms of stage, is constantly measured, and water samples are periodically taken. Since a strong inverse correlation commonly exists between stage and solute concentration, a number of approaches were developed to produce a continual estimate of discharge-weighted solute compositions (Likens et al., 1977; Zeman and Slaymaker, 1978). Integrating both the discharge and solute concentrations over a given time interval, commonly on an annual basis, and dividing this output by the geographical area of the watershed produces a solute flux $Q_{\text{watershed output}}$ (Equation 23), commonly expressed as moles ha$^{-1}$ yr$^{-1}$.

The weathering components associated with watershed discharge must be corrected for other potential sources and sinks within the watershed including atmospheric and anthropogenic inputs, biological cycling and changes in ion exchange processes in the soil. Such a relationship can be represented by the expression (Paces, 1986)

$$Q_{\text{weathering}} = Q_{\text{watershed output}} - Q_{\text{precipitation}} - Q_{\text{anthropogenic}} \pm Q_{\text{biologic}} \pm Q_{\text{exchange}}$$ (23)

Usually, for pristine watersheds, biologic and exchange reactions are assumed to be at steady state and the weathering flux is the difference between the watershed output and the precipitation input. In perturbed watersheds, the calculations become more complex due to agricultural inputs or changes in the exchange capacities due to watershed acidification.

The measurement of solute fluxes in surface water discharge is an indirect approach to estimating chemical weathering rates. Due to low mineral-to-fluid ratios and short residence times, minimal silicate weathering occurs in the streambed and the hyporheic environment. Rather, surface waters solutes represent discharges from other weathering environments that are spatially and temporally integrated by the watershed flux.

**Figure 18 Near Here**
The presence of multiple solute sources was demonstrated for variations in discharge from the Panola watershed in central Georgia USA (Hooper et al., 1990). As shown in Figure 18, variations in solute Si and Mg, are explained as a mixture of 3 end-member sources; a groundwater component contained in fractured granite, a hillslope component representing waters from soils and saprolites and an organic component consisting of near-surface runoff in the shallow soils. To further complicate the interpretation of the discharge flux, the relative proportions of these components vary seasonally. Hillslope waters dominate during the wet season (January to May). Groundwater dominates at low flow during seasonally dry periods, and the organic component is present only during intense storm events. Different weathering processes and rates are associated with each of these environments.

The above example serves as a cautionary note to the complexities involved in interpreting solute discharge fluxes and calculating weathering rates even in an intensely studied watershed. However, significant efforts, such as those contained in Trudgill (1995), are directed to resolving the various hydrologic and geochemical sources of watershed discharge using a number of computational approaches. The compilation of watershed solute fluxes is effective in establishing the impact of rock type, precipitation, temperature and other parameters on chemical weathering rates, e. g., Dethier (1986); Bluth and Kump (1994) and White and Blum (1995). Such fluxes are also used to calculate silicate weathering rates (Table 4).

5.04.4. NORMALIZATION OF WEATHERING TO REGOLITH SURFACE AREA

Weathering rates are fluxes defined by mass losses or gains across mineral surfaces in the regolith (Equation 1). On a fundamental level, the rate of reaction is directly proportional to the reactive surface area, which defines the density of reactive sites on a silicate surface at which hydrolysis reactions occur (Equation 2). While such site distributions are characterized in terms of ligand exchange sites and dislocation densities under laboratory conditions (Brantley and Olsen, this volume), natural weathering studies generally equate reactive surface area with the physical surface area of the weathering environment.

5.04.4.1 Definitions of Natural Surface Areas
Surface areas in natural weathering studies are commonly considered to be geographic, volumetric or mineral-specific. The weathering rate based on geographic surface area is defined as the mass of silicate mineral weathered per unit area of the Earth’s surface (e.g. hectares or km²). Generally this surface area is not corrected for aspect or slope of the terrain. Geographic surface areas are used extensively to describe weathering rates based on solute discharge in watersheds, which are normalized to basin areas ranging from small experimental catchments to the world’s rivers (Meybeck et al., 2004; Viers et al., this volume).

Weathering rates normalized to geographic surface area contain no information on the vertical dimension of the weathering environment, i.e. there is no distinction between weathering in a regolith that is one meter or ten meters thick. One approach in overcoming this problem is to employ a volumetric surface area, which is commonly done for ground water systems where weathering rates are defined either in terms of the volume of the aquifer. Commonly, surface areas contained in this volume are estimated based on the distributions of fracture surfaces or on sizes and distributions of pore spaces (Paces, 1973; Gislason and Eugster, 1987).

The more fundamental approach to addressing the physical dimensions involved in weathering is to characterize the surface areas of the individual minerals, i.e., the specific mineral surface area \( S_s \) (m² g⁻¹). The extent to which this specific surface area scales directly with the reactive surface areas in natural environments is a matter of considerable debate, particularly in regard to the accessibility of water. For unsaturated environments, such as those in most soils (Figure 13a), the wetted surface area may be considerably less than the physical surface area of contained mineral grains (Drever and Clow, 1995). In addition, surface areas of microscopic features such as external pits and internal pores may be associated with stagnant water that is thermodynamically saturated and not actively involved in weathering reactions (Oelkers, 2001).

5.04.4.2 Measurements of Specific Surfaces Areas

The scale of the measurement technique operationally defines the specific surface area of a mineral. Geometric estimates of surface area \( S_{geo} \) involve grain size analyses with physical dimensions commonly on the scale of millimeters to centimeters. Brunauer, Emmett and Teller
(BET) surface measurements $S_{BET}$ utilize isotherms describing low temperature sorption of $N_2$ or Ar on mineral surfaces. The scale of BET measurements, defined by atomic dimensions, is on the order of nanometers. As expected, specific surface areas determined by geometric techniques produce significantly smaller values of physical surface area than do BET measurements because the former technique does not consider microscopic irregularities on the external surface nor the internal porosity of mineral grains that have undergone significant weathering. Other techniques such as atomic force microscopy (Maurice et al., 2002) and interferometry (Luttge, 1999) have the potential to span the gap between the scales of geometric and BET surface area measurements.

BET surface areas are almost universally measured in experimental weathering studies using freshly ground and prepared minerals (Brantley and Olsen, this volume). BET surface areas are also commonly measured on samples of natural unconsolidated soils, saprolites and sediments. Alteration and destruction of the physical fabric of such materials by disaggregation is required for such measurements this producing uncertainties in the results. In addition, secondary clay and oxyhydroxides commonly coat natural silicate surfaces and contribute to the formation of mineral-organic aggregates (Tisdall, 1982). When not removed, these coatings can produce erroneously high surface areas. Alternatively, removing these phases, using mechanical and chemical methods, may expose additional silicate surfaces that are not present in the natural weathering environment.

In spite of the above issues, consistent trends of increasing surface area with increasing intensity of natural weathering have been established (Brantley et al., 1997). An example of this is shown in Figure 19a in which BET surfaces for primary minerals increase with increasing time in the Merced chronosequence (White et al., 1996). As indicated, the extent of this increase is dependent on the specific mineral phases, with more readily weathered plagioclase exhibiting greater increases than K-feldspar and quartz. Recently, small-angle and ultra-small-angle neutron scattering has been utilized to measure nm- to µm-scale surface area of natural shales, basalts, and granites (Jin et al., 2011; Navarre-Sitchler et al., 2012). Whereas the BET method only measures external or connected pores, neutron scattering also measures intra-particle (non-connected) porosity development and pore geometry. Although BET includes angstrom-scale roughness that is not detected by neutron-scattering methods, both methods gave similar results.
for basaltic rocks (Navarre-Sitchler et al., 2012). Similarly, both total and effective porosity and effective diffusion coefficients in weathering basalts have been determined using synchrotron X-ray microcomputed tomography and laboratory and numerical diffusion experiments (Navarre-Sitchler et al., 2009).

5.04.4.3 Surface Roughness

The surface roughness $\lambda$ is defined as the ratio of the geometric ($S_{\text{Geo}}$) and BET ($S_{\text{BET}}$) surface areas (Helgeson, 1971). For perfectly smooth surface with no internal porosity the two surface area measurements should be the same, i.e. $\lambda = 1$. For non-ideal surfaces of geometric spheres, the roughness can be related directly to the particle diameter $d$ and the mineral density $\rho$ such that

$$\lambda = \frac{S_{\text{BET}}}{S_{\text{Geo}}} = \frac{\rho d S_{\text{BET}}}{6}$$

White and Peterson (1990) calculated an average roughness factor of $\lambda = 7$ for a wide size range of fresh silicate surfaces. Surface roughness generally increases from these values with increasing chemical weathering. In tabulating available surface roughness for a number of naturally weathered silicate minerals (Figure 19b), White and Brantley (2003) proposed that silicate mineral roughness increases as a fractional exponent of time such that

$$\lambda = 1.13 t^{0.182}$$

This expression, shown by diagonal line showing the fit the plotted data in Figure 19b predicts an increase in surface roughing of about two orders of magnitude over time spans approaching a million years.

5.04.5. TABULATIONS OF WEATHERING RATES OF SOME COMMON SILICATE MINERALS

The diverse approaches described above have produced a number of published weathering rates that are not always comparable in terms of units and dimensions. In general,
weathering rates can be classified as being element or mineral specific. In the following sections, weathering rates based on geographic and volumetric surface areas are referred to as weathering fluxes and weathering based on specific surface areas are referred to as specific mineral weathering rates. In addition, chemical weathering is characterized in terms of kinetic rate constants or intrinsic rate constants which are weathering rates corrected for external variable influences such as solute pH and degree of thermodynamic saturation.

5.04.5.1 Elemental Weathering Fluxes

The most common examples of element-based rates are those reported for annual stream or river discharge and normalized to the watershed area. The relatively straightforward nature of these measurements, coupled with a significant amount of watershed research related to land management issues, has produced a large database describing such fluxes. A tabulation of these data is beyond the scope of the present paper and the reader is referred to previous compilations (Meybeck, 1979; Dethier, 1986; Bluth and Kump, 1994). Elemental weathering fluxes are equivalent to chemical denudation rates commonly defined as the sum of rock-derived base cations solubilized per unit area of geographic surface (Bluth and Kump, 1994; Drever and Clow, 1995). These rates also serve as a means to evaluate the importance of a number of environmental controls on chemical weathering including precipitation, temperature, vegetation and rock type. These topics are addressed briefly in later sections of this chapter as well as elsewhere in this volume (see Berner et. al., 2004; Meybeck, 2004; Granger and Riebe, this volume).

5.04.5.2 Mineral Weathering Fluxes

The alternative approach is to report silicate weathering fluxes on a mineral basis. As previously discussed, this requires distributing elemental fluxes among mineral phases using mass balance approaches described in this chapter and elsewhere (Bricker et al., 2004). Mineral flux data in the literature are less common than element-based data. Table 3 contains a limited tabulation of weathering rates for the common silicate minerals based on average annual watershed fluxes and geographic areas. Significantly more data are available for plagioclase
feldspar than for other mineral phases, which partly reflect a common occurrence in crystalline rocks. In addition, the rate of plagioclase weathering is the easiest to calculate, because of the conventional assumption that it scales directly with the Na discharge flux after correction for precipitation inputs. Weathering rates of other silicates are more difficult to determine from elemental fluxes because their major components are commonly derived from more than one mineral.

**Table 3 Near Here**

The reported weathering rates in Table 3 are normalized to the geographic surface area of the watershed but not to the relative proportions or surface areas of the specific mineral present. The presence of relatively large amounts of plagioclase in most igneous rocks accounts for the fact that the rates of plagioclase weathering, calculated on a watershed basis, are more rapid than other silicates such as hornblende, which is counter to Goldich's order of weatherability (Goldich, 1938).

### 5.04.5. 3 Specific Mineral Weathering Rates

Natural weathering rates, normalized to specific mineral surface areas, are reported in Table 4 for a number of common silicate minerals. Also included in the Table 4 are the ages of the weathering environment and parameters defining the physical surface area of the minerals. Large variations are apparent in the reported weathering rates for each of the minerals. For example, reported plagioclase rates vary from $4 \times 10^{-17}$ moles m$^{-2}$ s$^{-1}$ in the Davis Run saprolite in Virginia (White et al., 2001) to $1.5 \times 10^{-12}$ moles m$^{-2}$ s$^{-1}$ in the Plastic Lake watershed in Ontario Canada (Kirkwood and Nesbitt, 1991).

Rates based on geometric surface areas are generally more rapid than those based on BET measurements. This correlation, in part, explains age trends in the rate data. Rates for younger weathering environments are based primarily on watershed fluxes and geometric surface area estimates in the literature. In nearly all cases, these watersheds are developed on glaciated topographies developed over the last 12 kyrs. In contrast, weathering rates in older soils, varying in ages from 10 kyrs to 3,000 kyrs, are based on BET surface measurement techniques. In an attempt to reconcile these surface area differences, geometric surface areas were converted to
equivalent BET surface areas based on the roughness relationship shown in Figure 19b (Equation 25). The corrected rates are denoted in parentheses in Table 4.

Table 4 Near Here

5.04.6 TIME AS A FACTOR IN NATURAL WEATHERING

Discrepancies of about 2-4 orders of magnitude between silicate weathering rates calculated from laboratory experiments and those calculated from field data are well documented in the literature e.g., Schnoor (1990); White et al., (1996); White and Brantley, (2003). This difference, present in the data in Table 4, is shown in the plot of reaction rates for K-feldspars and plagioclase weathering derived from laboratory experiments and studies of natural systems (Figure 20). Time, plotted as years in the case of laboratory studies corresponds to the length of the experiments and in the case of natural systems, to the total duration of chemical weathering.

Figure 20 Near Here

Also shown in Figure 20, is a trend of declining weathering rates for natural systems of progressively increasing age. This has been previously documented in well constrained weathering systems notably soil chronosequences (Hodson et al., 1999; Taylor and Blum, 1995; Stewart et al., 2001, White et al., 2009). Regression fits to the K-feldspar and plagioclase data (dashed lines) produce the respective power rate laws

$$R_{Ksp} = 10^{-12.1}t^{-0.65}; \quad R_{plag} = 10^{-12.5}t^{-0.56}$$

that describe the progressive decrease in plagioclase weathering with time. Equation 26 is similar to a relationship developed by Taylor and Blum (1995) to describe the decrease in chemical fluxes in a suite of soils with time and is comparable to parabolic kinetics describing transport control in the hydration of obsidian and the development of rock weathering rinds (Coleman, 1981; Friedman et al., 1994). The time dependency of silicate weathering is a function of processes that are intrinsic to the silicate mineral and those extrinsic to the weathering environment. These factors will be discussed in subsequent sections of this chapter.

5.04.6.1 Comparison of Contemporary and Geologic Rates
The duration of chemical weathering in natural systems used as the time scale in Figure 20 is the same whether rates are based on solid state or solute weathering fluxes. However the actual time spans over which weathering are measured are very different. Solid-state mass differences commonly reflect weathering of over geologic time scales of thousands to millions of years \((t_{\text{solid}})\). The duration of chemical weathering reflected in solute compositions \((t_{\text{solute}})\) is equivalent to the residence time of the water in the regolith, commonly the time elapsed since initial recharge as precipitation. For most weathering environments such as soils, watersheds and shallow ground waters, solute residence times range from days to decades. Recent advances have significantly increased our ability to quantitatively measure the duration of weathering associated with both solid state and solute mass changes. Of particular importance is the use of cosmogenic isotopes such as \(^{36}\text{Cl}\), \(^{26}\text{Al}\) and \(^{10}\text{Be}\) in age dating geomorphic surfaces, the use of U-Th to quantify soil production rates; and the use of \(^{36}\text{Cl}\), \(^{3}\text{He}/^{4}\text{He}\) and chlorofluorocarbons to establish fluid residence times over time spans of years to tens of thousands of years (Plummer et al., 1993; Phillips and Castro, 2003; Granger and Riebe, this volume).

Comparing modern and past silicate weathering rates is important in addressing issues such as soil sustainability, climate change and global CO\(_2\) drawdown. Rates based on solute compositions are measurements of present day weathering that correlate with contemporary environmental conditions including hydrology, climate and vegetation. Weathering rates based on solid-state composition changes reflect average rates integrated over geologic time during which the conditions influencing weathering may have changed significantly.

Some workers have documented that present day base cation fluxes measured in North America and Northern Europe watersheds are significantly faster than long-term past weathering rates due to the impacts of acidic precipitation (April et al., 1986; Kirkwood, 1989; Kirkwood and Nesbitt, 1991; Land et al., 1999). Likewise, Cleaves (1993) found watershed solute discharge in the Piedmont of the eastern USA to be 2-5 times faster than for past periglacial periods represented by long-term saprolite weathering. He attributed these weathering rate differences to past periods of lower precipitation, colder temperatures and lower soil gas CO\(_2\). In contrast, Pavich (1986) concluded long-term weathering rates of saprolites in the Virginia Piedmont are comparable to current-day weathering rates based on stream solute fluxes. Rates of saprolite formation are also similar to current weathering rates in the Luquillo Mountains of Puerto Rico (White et al., 1998).
and in the Panola watershed in northern Georgia, USA (White and al., 2002). As the literature indicates, considerable debate exists regarding the extent to which contemporary fluxes correspond to increased weathering or result from other contributions such as enhanced cation exchange rates, deforestation and other parameters contained in Equation 23.

Under steady state weathering conditions, the solid state and solute rates $R_{\text{solid}}$ and $R_{\text{solute}}$ (Equations 3 and 4) must be equal and proportional to the respective mass changes with time, i.e.,

$$R_{\text{solid}} = R_{\text{solute}} = \frac{\Delta M_{\text{solid}}}{t_{\text{solid}}} = \frac{\Delta M_{\text{solute}}}{t_{\text{solute}}}$$

(27)

Based on the geometric interpretations summarized in Figure 3, the solute and solid-state weathering profiles should be directly related under steady state weathering conditions. Assuming constant weathering rates and surface areas, Equation 3 can be equated to Equation 4 such that (White et al., 2009)

$$\left[ \frac{q_{b}}{a} \right] \frac{b_{\text{solid}}}{b_{\text{solute}}} = 1$$

(28)

where the product of the ratio of the weathering velocities and inverse ratio of the weathering gradients is equal to one. Values greater than one represent faster contemporary rates relative to slower long-term rates and values less than one slower contemporary relative to long-term rates.

Figure. 21 Near Here

Solute and solid state weathering profiles for soils of the Santa Cruz chronosequence are compared, based on the respective slopes on the weathering profiles in Figure 21 (after White et al, 2009). Based on Equation 28, contemporary weathering rates in the younger terraces are about three times faster than the long term rates, while in the older terraces, they are comparable. As discussed by White et al. (2009), a number of environment factors may be responsible for these differences.

5.04.7 FACTORS INFLUENCING NATURAL WEATHERING RATES
Weathering rates are dependent on a number of factors which can be classified as either intrinsic or extrinsic to a specific mineral (White and Brantley, 2003). Intrinsic properties are physical or chemical characteristics of a mineral such as composition, surface area and defect densities. If intrinsic properties dominate weathering, such characteristics should be transferable between environments, e.g., laboratory and field rates of the same mineral should be comparable. Extrinsic features reflect environmental conditions external to the silicate phase that impact chemical weathering such as solution composition, climate and biological activity (e.g., Berner, 2004). These processes are dependent on external environmental conditions that are difficult to recreate fully under laboratory simulations.

5.04.7.1 Mineral Weatherability

Mineral composition and structure are the primary intrinsic factors controlling weathering rates. Based on early weathering studies, Goldrich (1938) observed that the weathering sequence for common igneous rocks in the field was the reverse of Bowen’s reaction series that ranked minerals in the order of crystallization from magma. Amphiboles and pyroxenes are expected to weather faster than feldspars which weather faster than quartz. In addition, field data suggest that volcanic glasses weather an order of magnitude faster than crystalline minerals of comparable composition (Gislason et al., 1996).

Although no fundamental method exists for predicting the weathering order of all silicate minerals, certain trends in rates between minerals are apparent. Silicate weathering is commonly viewed as a ligand exchange process with the metal ions bonded in the mineral structure. The rates are dependent on the relative strengths of coordinated metal ions within the mineral structure relative to the strength of the metal ligand bond. Casey and Westrich (1992) originally showed that for simple compositional series, such as olivines, the dissolution rate decreased with the increase in the metal valence state. Evidence also indicates that the relative weathering rates of multi-oxides such as feldspars approximate the relative dissolution rates of the single oxide components (Oelkers, 2001). A more detailed discussion of the relationship between weathering mechanisms and rates is presented elsewhere in this volume (Brantley and Olsen, this volume).
For structurally complex minerals undergoing incongruent or stepwise weathering in the natural environment, the relative rates become very dependent on specific reaction pathways. In case of micas, for example, biotite and muscovite are structurally similar but weather at very different rates as shown for the example of residual biotite and muscovite weathering in the saprolite developed on the Panola Granite (White et al., 2002). Biotite exhibits a progressive loss of K and an increase in the Al/Si ratio that correlates with increasing weathering intensity and decreasing depth in the profile (Figure 22a). These changes are driven by the relatively rapid oxidation of ferrous Fe in biotite (Amonette et al., 1988). As shown by the electron backscatter image in Figure 22b, this reaction produces epitaxial replacement of biotite by kaolinite. In contrast, the muscovite, which is structurally similar, but contains low concentrations of Fe weathers very slowly, exhibiting no K loss in the Panola saprolite (Figure 22a). The dramatic differences in the behavior of mica minerals emphasize the importance of mineral-specific reactions in the weathering environment.

Mineral surfaces are heterogeneous substrates possessing compositional and structural features that may differ from those of the bulk mineral phase. Compositional differences within single mineral grains due to zonation and exsolution can influence reaction rates. As predicted by the Bowen reaction sequence, the crystallization of plagioclase phenocrysts often produces calcic cores surrounded by more sodic rims. During the reverse process of chemical weathering, the plagioclase cores weather more rapidly, producing preferential release of solute Ca relative to Na (Clayton, 1986). Such incongruent dissolution is a process that has been invoked to explain the commonly observed excess solute Ca to Na ratios in watershed fluxes relative to that predicted from the bulk plagioclase stoichiometry (Stauffer, 1990).

Incongruent weathering also occurs at exsolution features. Detailed SEM studies of perthitic textures of naturally weathered feldspars by Lee and Parsons (1995) showed that the etch density was strongly dependent on the composition of these exsolution features, i.e., the Na component dissolved more rapidly than the K component. The highest densities of defect structures are also created along the strained lamellae. Weathering rates of specific minerals may therefore be dependent on the crystallization history of igneous rocks as well as the effects of tectonics and deformation on defect formation.
Weathering acts on mineral surfaces by decreasing the overall surface free energy by selectively dissolving more soluble components and attacking structural defects and dislocations. With continued weathering, the overall surface energy and the corresponding weathering rate may decrease. The progressive occlusion of the reactive mineral substrate by secondary clays and Fe- and Al oxides, the formation of depleted leached layers and the adsorption of organic compounds, have also been proposed as mechanisms to decrease surface reactivity with time. Whether these secondary coatings represent effective barriers to the transport of reactants and products from the reactive silicate surface is still actively debated.

5.04.7.2 Solute Chemistry and Saturation States

Of the extrinsic factors influencing natural weathering rates, solute compositions have the most direct impact. Chemical weathering is ultimately dependent on the concentrations of reactants which complex with and detach the oxygen-bonded metal species in the silicate structure (Casey and Ludwig, 1995). As documented by numerous experimental studies, the principal species involved in this reaction are hydrogen ions, although other complexing agents such as organic acids can participate in this process (see Brantley, 2004; this volume). In contrast, some solute species, such as Al and Na ions, inhibit experimental weathering rates by interfering with and competing with the ligand exchange processes (Oelkers and Schott, 1995; Stillings et al., 1996).

Experimental rates of silicate dissolution decrease as solutions approach thermodynamic equilibrium (Burch et al., 1993; Taylor et al., 2000). The saturation state \( \Omega \) is defined as the product of the solute activities (IAP) divided by the saturation constant of the specific mineral \( K_s \) and is commonly related to the net free energy of reaction \( \Delta G \) (kJ mole\(^{-1}\)) by the relationship

\[
\Omega = \exp \left( \frac{\Delta G}{R' T} \right) \tag{29}
\]

where \( T (K^\circ) \) is the temperature and \( R' \) is the gas constant. When the system is undersaturated, i. e., \( \Omega \) is < 1, \( \Delta G \) is negative, leading to dissolution. At a \( \Omega = 1 \), thermodynamic saturation is
achieved and \( \Delta G = 0 \). If \( \Omega > 1 \), the system is supersaturated, \( \Delta G \) is positive and precipitation may commence.

Based on transition state theory, the simplest relationship between the reaction rate and the solute saturation state is represented as (Nagy et al., 1991)

\[
R = k \left[ 1 - \Omega^n \right]^m
\]

(30)

where \( k \) is the intrinsic rate constant and \( m \) and \( n \) are orders of reaction. In strongly undersaturated solutions (large negative values of \( \Delta G \)), net detachment reactions dominate over attachment reactions, the dissolution rate is independent of solute concentration and \( R \) is directly proportional to the intrinsic rate constant. At near saturation (small values of \( \Delta G \)), Equation 30 reduces to a form in which \( R \) becomes linearly dependent on \( \Delta G \). At equilibrium \( (\Delta G = 0) \) the weathering rate is zero. Several kinetic rate laws have been proposed to describe aluminosilicate dissolution in terms of reaction affinity or the saturation state of the solution (e.g., Equation 30). These include the transition state theory (TST) approach outlined in Equation 30 (Lasaga, 1984), the Al-inhibition model (AIM) (Oelkers et al., 1994; Gautier et al., 1994; Carroll and Knauss, 2005 and the parallel rate law approach (PRL) (Burch et al., 1993; Hellmann and Tisserand, 2006). An evaluation of several rate laws was applied to the weathering profiles in the Santa Cruz terraces using the reactive-transport model Crunchflow (Figure 10; Maher et al., 2009).

Calculations involving mineral saturation (\( \Omega \) in Equations 29 and 30) are dependent on accurate characterization of the thermodynamic states of the reactants and products and are commonly calculated using speciation codes (see Nordstrom, this volume). Although the equilibrium constants for many simple primary silicates have been determined, thermodynamic data do not exist for many complex silicates or for solid solutions. In addition apparent thermodynamic supersaturation of silicate minerals in many soil pore waters result from excessive values for total dissolved Al. In reality, much of this Al is complexed with dissolved organics in shallow soils and does not contribute to the thermodynamic saturation state of silicate minerals. Solubility calculations involving low dissolved organic concentrations in deeper soil
horizons and in groundwater appear to produce much clearer equilibrium relationships (Stefansson and Arnorsson, 2000; Stefansson, 2001).

Natural weathering commonly involves much longer times and smaller solution/solid ratios than obtained in experimental studies. Natural weathering may therefore occur much closer to thermodynamic equilibrium. This difference in saturation states may explain two common discrepancies observed when comparing experimental and natural weathering rates. As has been frequently noted by others and documented in detail in Figure 20, natural weathering rates are commonly several orders magnitude slower than experimental rates. Secondly, the relative weatherability of minerals in the natural environment often differs from that predicted on the basis of experimental dissolution rates. For example, in a review of experimental feldspar dissolution studies, Blum and Stillings (1995) concluded that under neutral to acidic pH conditions, the rates of sodic plagioclase and K-feldspar dissolution were essentially the same. However, K-feldspar commonly is much more resistant to dissolution than is plagioclase during natural weathering (Nesbitt et al., 1997).

**Figure 23 Near Here**

Weathering of the Panola Granite is an extreme example of the relative weathering rates of feldspars (White et al., 2001). As shown by mass balance calculations (Figures 3 and 4), kaolinization of plagioclase occurs at depths to 10 m in the granite regolith (Figure 7). This is evident in SEM images (Figure 23a) in which, except for residual rims, plagioclase grains are completely replaced by kaolinite. In contrast, K-feldspar in the immediate proximity of plagioclase grains remains pristine and unaffected by weathering. The significant difference in feldspar weathering rates at depth in the Panola was explained by White et al. (2001) by the difference in their respective thermodynamic saturation states (Figure 23b and c) and not by their relative reaction kinetics which are similar (Figure 20a and b). Soil pore waters are generally undersaturated with respect to both plagioclase and K-feldspar (Figures 23b and c). In contrast, groundwater in the underlying granite bedrock is saturated with K-feldspar but undersaturated with more soluble plagioclase. Equation 30 predicts that plagioclase will weather in contact with groundwater while K-feldspar will remain stable.
Kaolinite and other secondary minerals are often treated as passive by-products of primary mineral dissolution with infinite rates of precipitation. In reality, secondary clay formation can draw down solute concentrations, particularly Al, in turn providing a substantial driving force for dissolution of primary silicates (Zhu, 2005). Soil profile development in the Santa Cruz terraces is characterized by the formation of kaolinite-rich argillic horizons that are more intensely developed with increasing terrace age (White et al., 2008). The kaolinite profiles in the argillic horizons are approximately the inverse of the plagioclase profiles, with kaolinite accumulating at increasingly depths over time due to the depletion of primary minerals above and the downward transport of aqueous weathering products (Figure 24). These results indicate that Al is largely conserved.

Both plagioclase and K-feldspar weathering profiles are affected by the incorporation of kaolinite precipitation kinetics into the Crunch Flow model for the Santa Cruz terraces (Figure 24, Maher et al., 2009). Although the shape of the kaolinite profile is affected by the reaction fronts of the dissolving minerals, kaolinite precipitation is critical for sustaining primary mineral dissolution. Figure 24 shows the effects of a factor of 5 increase and decrease in the rate constant for kaolinite precipitation on its profile development in SCT 5, and the corresponding impact on the feldspar weathering profiles.

**Figure 24 Near Here**

Changes in the rate of kaolinite precipitation do not affect the primary mineral kinetic rate constants or weathering gradients. However, an increase in the kaolinite precipitation rate removes weathering products from solution and therefore results in an increase the weathering velocity of the primary minerals (Figure 24). A factor of 10 increase in the rate of kaolinite precipitation is equivalent to increasing the pore water flow rate by a factor of 1.5 or of adding an additional 100 ka to profile development. The variables are thus inversely correlated in the model (for the same fit to the data). Increasing kaolinite precipitation increases the total mass loss and the amount of mineral dissolved during weathering but will not substantially change the gradients of the saturation state or weathering profiles over depth as the later are controlled by the intrinsic rate constants. For example, to fit the data at higher flow rates requires only a slower
rate constant for kaolinite precipitation, but does not require appreciable changes to the primary mineral dissolution rates (Maher et al, 2009).

5.04.7.3 Coupling the Effect of Hydrology and Chemical Weathering

Thermodynamic saturation is dependent on solute concentrations, which in turn, are controlled by the volume and residence times of fluids moving through the weathering environment. The roles of hydrology and chemical weathering are commonly coupled in a weathering regolith and can be viewed as co-evolving as the intensity of the weathering increases. This effect is evident both in the initial phases of chemical weathering in bedrock environments and development of argillic horizons in older soils.

The schematic in Figure 25a shows the hypothetical weathering of bedrock to regolith. A zone of “pristine rock” is present at depth (Zone I). At some point, meteoric fluids are introduced into the bedrock and aqueous species react with one or more mineral phases. The products of this reaction begin to be transported out of the bedrock, creating mass depletion, slightly increased porosity and secondary fluid fluxes $q_s$ (equivalent to $q_h$) that are greater than the flux in the pristine bedrock $q_p$ (Zone II, Figure 25a). Under these conditions, however, the limited volume of pore water rapidly saturates thermodynamically with respect to the reacting mineral. Weathering rates at this stage of regolith development proceed very close to equilibrium and are thus limited by rates of transport through the weathered rock rather than by the kinetic rates of reaction of the primary minerals.

Figure 25 Near Here

With increasing time, an increasing weathering intensity and mass depletion increases the secondary hydraulic conductivity such that the fluid fluxes becomes sufficiently large that one or more of the most soluble reactive minerals becomes thermodynamically undersaturated (Zone III, Figure 25a). Weathering of these minerals is now dependent on the kinetic rate of reaction and not on the fluid transport rate $q_h$. However, mineral phases with lower solubilities will continue to remain thermodynamically equilibrated. Finally, sufficient mass transfer occurs with increasing fluid flux ($q_h \gg q_p$) and pore water volume to the extent that all the primary minerals become unsaturated (Zone IV, Figure 25a). As shown in the diagram, weathering is thus expected to
progress from a regime that is limited by fluid transport (transport-limited) to a regime that is described by mixed limitation (transport- and kinetic-limited to a regime that is described by kinetic limitation (Figure 25a).

The relative rates of plagioclase and K-feldspar weathering to form kaolinite in the Panola saprolite is an example of the coupled effects shown in Figure 25a. This process was modeled by White et. al. (2001) as a coupled relationship between weathering rates and the development of secondary permeability (Figure 25b). At the initiation of weathering, the matrix permeability and fluid flow in the fresh granite is extremely low ($q_p = 10^{-5}$ m yr$^{-1}$), placing severe constraints on the mass of feldspar that can dissolve before becoming thermodynamically saturated. Under such conditions, weathering is limited by the availability of water and not by the kinetic rate of feldspar weathering.

Over long times, slow rates of transport-limited weathering occurs, resulting in mass loss from the granite (Figure 25b). Based on density estimates, the conversion of plagioclase to kaolinite (Equation 2) produces a porosity increase of about 50%. Such a situation is evident in the thin section of the Panola Granite (Figure 23a) showing the development of secondary porosity. This change in porosity slowly increases the secondary fluid flux, plotted as the ratio of $q_s/q_p$ in Figure 25b. Increased pore water volumes accelerate saturation-limited weathering and produces greater porosity and even high fluxes. This coupled feedback accelerates plagioclase weathering, which gradually shifts from a transport limited to a kinetic limited reaction (Figure 25a and b). At $q_s/q_p$ ratios > 150, plagioclase weathering becomes completely controlled by kinetics and no longer reflects additional increases in conductivity.

The rate of K-feldspar weathering shows a comparable transition from transport to kinetic control but at significant higher secondary $q_s/q_p$ flux ratios primarily due to its lower solubility (about 400 times less soluble than plagioclase) and not to slower reaction kinetics. Concurrent plagioclase dissolution enhances this effect by producing solutes, principally Si, which further repress K-feldspar dissolution by increasing its saturation in the pore waters. The observation in thin section (Figure 23a) that plagioclase is almost completely weathered at depth in the Panola Granite while K-feldspar remains essentially pristine sets the range of the secondary to primary fluid fluxes at the specific depth in the Panola Granite at approximately $q_s/q_p = 150$ (Figure
5.04.7.3.1 Low Permeability

In order to weather massive, non-porous bedrock, such as a granitic pluton (Zone I in Figure 25a), reacting fluids need access to the weatherable minerals. Initiation of weathering in such rock is thus dependent not only on chemical reactivity, but also transport of reacting fluids and the formation of secondary porosity. White et al. (1999; 2005) found that accessory calcite is ubiquitous in granitoid rocks. Calcite distributions in the Panola Granite are shown in the cathodoluminescent photomicrograph in Figure 26a, displaying disseminated calcite internally distributed in a K-feldspar grain. The comparison of weathering profiles for CaO, dominated by plagioclase and trace amounts of calcite suggest that advancement of the calcite weathering front creates sufficient secondary porosity to initiate plagioclase but not K-feldspar weathering in the Panola bedrock (Figure 25b).

**Figure 26 Near Here**

In other cases, initial porosity may be created by reaction-driven fracturing initiated, for example, by the diffusion of oxygen into the bedrock and the subsequent oxidation of ferrous silicate minerals and bedrock fracturing (Fletcher et al., 2006). A spheroidally weathering interface, such as in the low permeability quartz diorite bedrock of the Rio Icacos watershed in Puerto Rico, presents an ideal environment for studying porosity development by reaction-driven fracturing. Spheroidal weathering is a well-known, but poorly understood, type of exfoliation that has been attributed to chemical weathering (; Farmin, 1937;; Ollier, 1971; Fletcher et al., 2006; Buss et al., 2008). The process begins when bedrock weathers along the surfaces of joint planes, rounding off corners to form, in-situ, boulders called corestones. Corestones then fracture, forming concentric layers called rindlets (Bisdom, 1967; Ollier, 1971; Fritz and Ragland, 1980; Turner et al., 2003; Buss et al., 2005; Buss et al., 2008). A set of rindlets (from
corestone to saprolite) comprises the weathering rind, also referred to as a rindlet zone (Figure 27).

**Figure 27 Near Here**

The rindlet zones in the Río Icacos quartz diorite are comprised of sequences (~0.2 – 2 m thick) of rindlets, each about 2.5 cm thick, which are only slightly weathered relative to the parent corestones (Figure 27). The hand-friable outer rindlets (at the saprolite interface) can be described as saprock or protosaprolite, a material intermediate between saprolite and bedrock. Corestone-rindlet complexes that remain in place at depth eventually weather to saprolite. Where rindlet zones are exposed by erosion, they tend to slough off, leaving bare corestones.

The physical expansion of minerals during chemical weathering has been identified as a potential cause of the spheroidal weathering (Blackwelder 1925; Larsen, 1948; Simpson, 1964; Eggler et al., 1969; Isherwood and Street, 1976; Begle, 1978; Chatterjee and Raymahashay, 1998; Fletcher et al., 2006; Buss et al. 2008). In many of those studies, hydration reactions such as the formation of vermiculite from biotite were put forward as expansion mechanisms. However, hydration reactions are unlikely in very low permeability rocks. An alternative expansion-inducing reaction mechanism was proposed by Buss et al. (2008) for the spheroidal fracturing. Using synchrotron X-ray microprobe fluorescence imaging and XANES, Buss et al. (2008) identified the oxidation of Fe(II) in biotite as the first weathering reaction occurring in a corestone from the Rio Icacos watershed. Oxidized biotite in the Rio Icacos weathering profiles is characterized by an expansion in the d(00l) direction from 10.0 Å to 10.5 Å (Dong et al., 1998; Murphy et al., 1998). This small expansion builds up elastic strain energy within the corestone. The corestone fractures when the elastic strain energy density reaches the fracture surface energy, creating a rindlet, as reproduced using a 1D numerical model by Fletcher et al. (2006) (Figure 28).

Similarly, a 2D numerical model was utilized to demonstrate the propagation of dendritic and network fracture patterns by high-temperature devolitalization reactions (Malthe-Sørenssen et al., 2006). In that study, a volatile reaction product is released from the solid via diffusion or evaporation with a net volume reduction. The rate of fracture propagation is controlled by the rate of kinetics of diffusion or evaporation. The change in concentration due to the reaction
produces a stress on the edge of the solid (or a preexisting fracture), producing a new fracture when the stress intensity exceeds a critical stress value. Røyne et al. (2008) adapted the model of Malthe-Sørenssen et al. (2006) to the case of spheroidal weathering by including a hypothetical reaction-driven expansion. The resulting model reproduced the hierarchical fractures that round and subdivide corestones.

In the Rio Icacos corestones, the fracture-controlling reaction, oxidation of Fe(II) in biotite, is initiated when dissolved oxygen diffuses into the corestones; thus the weathering rate is dependent upon the concentration of oxygen in the pore waters (Buss et al., 2008) and the thickness of the rindlets is related to the characteristic length scale of diffusion. The pore water oxygen concentration is expected to vary with regolith thickness, creating a positive feedback between erosion and weathering rates that may maintain profiles at steady-state over geologic time (Fletcher et al., 2006).

The rindlet-bounding fractures create initial permeability in the Rio Icacos bedrock, acting as conduits for the rapid infiltration of water. As weathering progresses within the rindlet zone, micro-cracks form within individual rindlets. Chemical weathering along rindlet-bounding fractures and micro-cracks creates additional porosity as mass is lost by the dissolution of plagioclase, hornblende, chlorite, and apatite. Fractures also facilitate the rapid removal of solubilized weathering products (e.g., Na, Ca). Thus the creation of permeability in the Rio Icacos bedrock is initiated by reaction-driven fracturing controlled by diffusion of O$_2$ into the unweathered rock. Further permeability is created by chemical weathering (in the rindlet zone and overlying saprolite), which is largely controlled by advective transport of reacting fluids within the fractures and pore spaces.

**Figure 28 Near Here**

### 5.04.7.3.2 High Permeability

High permeability weathering environments (Zone IV in Figure 25a) can be represented by primarily porosity such as in sandy sediments such the Santa Cruz beach deposits or by secondary porosity in saprolites such as at Panola and Rio Icacos. Under such conditions fluid flow is less dependent on the physical properties of the soil or rock, such as porosity and tortuosity, but more on the availability of water. As indicated in Figure 13, high degrees of
fluid saturation produce high fluid conductivities resulting in the infiltration of large amounts of water. Low degrees of saturation produce very low conductivities resulting in stagnant pore water conditions. Many porous soils are characterized in terms of field capacity, commonly near 50% saturation where conductivities are diminished to the point at which pore waters for practical purposes is not longer mobile. The magnitude of fluid flow and chemical weathering rates and profile development are linked by chemical thermodynamic constraints. A greater volume of pore water or groundwater moving at faster rates permits deeper penetration of the solute weathering front before solutes become thermodynamically saturated with respect to the reacting mineral.

The oldest terrace (SCT5) of the Santa Cruz chronosequence provides an example of a high permeability regolith (Figure 29). Two primarily variables were considered in the spreadsheet model used to fit the feldspar weathering profiles (White et al., 2008) the fluid flux $q_h$, and the rate constant $k_r$. The amount of water that moves through a terrace, i. e., the hydraulic flux $q_h$, was determined to be the principal control on the plagioclase weathering gradient $b$, and the total mass of plagioclase reacted $\Delta M_{plag}$. The strong sensitivity of the SCT 5 plagioclase profile to flow rate is shown in Figure 29a, in which the best fit value $q_h = 0.058 \text{ m yr}^{-1}$ (solid line) is arbitrarily increased and decreased by factors of 2 and 4 (dashed lines). Slower fluxes ($q_h/2$ and $q_h/4$) produced shallower weathering profiles (lower values of $b$, in Figs. 3a and 29a) because pore waters became thermodynamically saturated with plagioclase at shallower depths (Figure 15a). Increasing the flow rates ($2q_h$ and $4q_h$), in contrast, progressively deepened the plagioclase profiles thereby increasing the depths at which plagioclase became saturated (Figure 29a). The flow rates also largely controlled the total amount of plagioclase weathered out of the SCT 5 profile.

Figure 29 Near Here

Unlike for pore water flow, increases in the rate constant $k_r$ did not significantly affect the total amount of plagioclase reacted in the profile ($\Delta M$ in Equation 17). Graphically, this is apparent in Figure 29b, where increases in $k_r$ “rotate” the weathering gradient $b$, upward at higher residual plagioclase concentrations, increasing the weathering intensity at shallower depth but also decreasing it at greater depths. The net result is that the amounts of plagioclase reacted underneath the different curves in Figure 29b are about the same. These results are contrasted

58
against large changes in the amount of plagioclase reacted by comparable increases or decreases
the fluid flow rate (Figure 29a).

These results indicate that chemical weathering rates are very sensitive to the availability
of water which in many natural systems can be a significant variable. As shown in Figure 13,
large changes in moisture contents, certainly greater than those suggested in Figure 29a can
occur on a seasonal basis such as during cyclic wetting and drying associated with dry
Mediterranean climates such as Santa Cruz or during seasonal snow melt in other climates.
Moisture variability associated with decadal scale draughts or even longer term climate change is
expected to have profound effects on weathering in these high permeability environments.

5.04.7. 4 Role of Climate on Chemical Weathering

The term “weathering” implies that chemical weathering is related to climate. This
relationship is important both from the standpoint of the potential long term feedback during much
of the Earth’s history as well as the current impacts on changes in nutrient cycling produced by
present day CO₂ inputs to the atmosphere. The importance of climate relative to other controls on
weathering, in particular, topography and tectonics, remains controversial (Ruddiman 1997; and
papers therein). Examples of contrasting results comparing weathering rates in small scale
catchments are contained in White et al. (1995) Oliva et al. (2003) and Gislason et al., (2009)
who found climate to be the most important control while Riebe et al. (2001; 2004) determined
that topography and physical erosion were the dominant factors.

Despite the ongoing debate about the primary control, it is clear that chemical weathering
rates are functions of multiple, interdependent parameters including climate, physical erosion,
vegetation, and regolith age. For example, physical erosion generally increases with
precipitation, exposing fresher mineral surfaces and increasing weathering rates. Likewise,
higher rainfall may promote greater plant productivity, increased soil CO₂ and more dissolved
organic acids, all of which tend to vary systematically with climate. Furthermore, the relative
dependence of weathering rates on climatological or physical parameters may vary according to
the weathering regime (West et al., 2005).
A definitive study would involve a weathering environment that has undergone consistent sustained climate change. Generally, the long-term data required for such a study are not available and surrogate weathering studies comparing spatially separated climatic regimes comprise the majority of the relevant literature. The utility of such comparisons depends on the ability to isolate the effects of climate from other variables that influence chemical weathering including lithology, geomorphology and vegetation. Some of these parameters often correlate with climate, making the isolation of individual variables difficult. A recent study on 8 nearly pristine, basaltic catchments in Iceland undertaken over 44 years documented distinct increases in both chemical and physical weathering fluxes that correlate with increasing mean annual temperature (MAT) and runoff over the same time period (Gislason et al., 2009). The ability to isolate climate effects decreases as the scale of the weathering process increases. For example, a number of studies comparing weathering rates in soils and small catchments have found a significant climate effect (Velbel, 1993; White and Blum, 1995; Dessert et al., 2001). In contrast, comparison of solute concentrations and fluxes originating from large scale river systems most often fail to detect a climate signature (Edmond et al., 1995; Huh et al., 1998).

5.04.7.4.1 Temperature

The effect of temperature on weathering is the easiest climate parameter to predict on a fundamental basis. The rates of most chemical reactions, including silicate hydrolysis, increase exponentially with temperature according to the Arrhenius expression. This relationship can be represented as the ratio of reaction rates $R/R_o$ at different temperatures $T$ and $T_o$ ($°K$) (Brady, 1991; Brady and Carroll, 1994)

$$\frac{R}{R_o} = \exp \left[ \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_o} \right) \right]$$

(31)

The activation energy $E_a$ (kJ mole$^{-1}$K$^{-1}$) for dissolution of most common silicate minerals varies between 50 and 120 kJ (Brady, 1991; Casey and Sposito, 1992; White et al., 1999). Equation 31 predicts that rates should increase by about an order of magnitude between 0 and 25°C, the temperature range for most natural weathering environments. If temperature were the only
variable in weathering, the effect should be readily observable when comparing weathering environments at substantially different temperatures.

In addition to the temperature control on mineral weathering kinetics, the effect of temperature on the thermodynamic saturation state of a water-rock system is also an important control on weathering. This relationship is expressed via the van’t Hoff equation, which relates the equilibrium constant to the enthalpy ($\Delta H$) and temperature.

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2}$$

In a weathering-limited regime, where weathering can be considered to be relatively far from equilibrium (see section 5.04.7.5 The Role of Physical Weathering), chemical weathering rates are related to both the activation energy and the enthalpy of dissolution (Lebedeva et al., 2010). In the transport-limited regime, where weathering occurs closer to equilibrium, the temperature dependence on chemical weathering is thermodynamically controlled (Equation 32) and the kinetics of mineral weathering reactions do not affect the weathering fluxes that are observed.

**Figure 30 Near Here**

Temperature effects on the rate of chemical weathering are observed in many well-characterized environments. Velbel (1990; 1993) estimated elevation-dependent temperature differences in the Coweeta watershed in North Carolina, USA (10.6 to 11.7 °C) and calculated an activation energy of 77 kJ mol$^{-1}$ for plagioclase weathering. Dorn and Brady (1995) used plagioclase porosity formed by etch pitting in Hawaiian basalt flows at different elevations and temperatures (12.5 to 23.3 °C) to calculate an activation energy of 109 kJ mol$^{-1}$ (Figure 30a).

Williams et al. (2010) reported a correlation between Na depletion and temperature in 10-13 ky soils developed on Peoria loess deposits in a north-south transect spanning about 12 degrees of latitude and a range of temperature and precipitation regimes along the Mississippi River and calculated an activation energy of 75±14 kJ mol$^{-1}$ for albite dissolution.

On a much shorter timescale, Gislason et al. (2009) observed a relationship between temperature and chemical weathering flux in 8 basaltic catchments in Iceland over 44 years,
during which time the temperatures varied by 3.2 to 4.5 °C. They calculated activation energies (24–86 kJ mol\(^{-1}\)) that were higher than those measured on basaltic glasses in the laboratory, suggesting that other temperature-dependent factors, such as runoff, also enhance chemical weathering rates. Indeed, runoff was found to increase 6-16% for each degree of temperature increase over the 44 years of the study and to correlate positively with chemical weathering fluxes, which increased 4-14% for each degree of temperature increase (Gislason et al., 2009). Dessert et al. (2001) and Louvat and Allegre (1998) calculated an \(E_a\) of 42 kJ mol\(^{-1}\) for basalt weathering (2 to 27 °C) from a compilation of river fluxes (Figure 30b).

### 5.04.7.4.2 Precipitation and recharge

A number of studies have observed a linear correlation between precipitation or runoff and solute fluxes or chemical denudation rates (Dethier, 1986; Dunne, 1978; Stewart et al., 2001; Gislason et al., 2009). The relationship between solute Si fluxes and runoff of the large watershed data set plotted in Figure 31, shows comparable relationships for granitic and basaltic rock types (Bluth and Kump, 1994). As pointed out by Drever and Clow (1995), mineral surfaces undergo weathering only in the presence of liquid water. Increases in precipitation increase regolith recharge and the wetted surface areas of minerals, thereby promoting increased weathering. In addition, increased water flow increases the rates at which reactants, such as dissolved CO\(_2\) and organic acids, are flushed through the system. Finally, when increased precipitation leads to increased infiltration, the solute concentrations of pore waters in the regolith are diluted, which decreases thermodynamic saturation (Oliva et al., 2003).

**Figure 31 Near Here**

### 5.04.7.4.3 Coupling climate effects

In order to explain anomalously rapid rates of chemical weathering in upland topical watersheds such as in Puerto Rico and Malaysia, White and Blum (1995) proposed a coupled climate effect in which the solute fluxes were proportional to the product of a linear precipitation function and an exponential temperature function such that
Equation 33 was fitted to data for well-characterized upland catchments underlain by granitoid rocks. A 3-dimensional plot generated for Si fluxes is shown in Figure 32. The net predicted effect is to reinforce weathering in watersheds with both high temperatures and precipitation and to decrease weathering fluxes in watersheds with low temperature and precipitation. This conclusion is in agreement with Meybeck (1994) who showed that maximum concentrations of dissolved species from chemical weathering occur in rivers draining humid mountainous terrains and that minimum fluxes occur in arid and arctic rivers.

**Figure 32 Near Here**

Riebe et al. (2004) (also see Granger and Riebe, this volume) failed to find a direct correlation between precipitation or temperature and chemical weathering rates in 42 granitic catchments, although positive correlations were seen between the chemical weathering index, CDF, and both climate parameters. Von Blanckenburg (2006) suggested that these results demonstrate that although temperature and precipitation promote chemical weathering, external controls on weathering rates are dominated by tectonic forcing. It has also been proposed that the relative importance of climate versus tectonic forcing on weathering rates depends on the denudation regime of the individual catchments as discussed below (West et al., 2005; Gabet and Mudd, 2009).

### 5.04.7.5 Role of Physical Weathering

The role of physical weathering, or erosion, on weathering profile development was discussed in Section 5.04.3.1.3. More fundamentally, chemical weathering, in combination with physical erosion, are the processes that cycle elements globally. Berner and Berner (1997) estimated that the combined (physical + chemical) denudation rate of the continents is 252 tons km\(^{-1}\) y\(^{-1}\) while the average chemical denudation rate is about 20% of that value. As expected, the absolute rates and relative ratios of physical to chemical weathering are strongly scaled to differences in topography. For example, the percentage of chemical to physical denudation rates
for watersheds of high relief such as the Ganges River, which drains the Himalayas, is less than 10% but approaches 45% for lowland rivers such as the Congo River. Global compilations of denudation rates including data from the steep, but tectonically quiescent, Sri Lanka have shown that tectonic activity, rather than high relief alone, produces the high physical denudation rates seen in many mountainous watersheds (von Blanckenburg et al., 2004; 2006). Several researchers have identified a correlation between chemical weathering rates and total denudation or physical erosion rates (Riebe et al., 2004; West et al., 2005; von Blanckenburg, 2006; Dixon et al., 2009) from which they infer that processes that control or enhance physical erosion, such as uplift, also control chemical weathering rates.

Physical weathering can enhance rates of chemical weathering by exposing fresh mineral surfaces to attack by water. In turn, chemical weathering can increase rates of physical weathering by reducing bedrock coherence. This coupling between physical and chemical weathering is directly observed in many field sites. In the case of the spheroidally weathering quartz diorite in the Rio Icacos watershed in Puerto Rico, oxidative weathering of biotite drives initial fracturing of the bedrock, providing conduits for water to access minerals such as plagioclase (Buss et al., 2008). Continued mineral dissolution leads to disaggregation and the formation of saprolite, which is then susceptible to erosion via landsliding during periods of heavy rainfall (Larsen and Torres-Sanchez). In the basaltic catchments in Iceland, both physical and chemical erosion increased over the 44 years of the study (Gislason et al., 2009). The physical erosion rates in the glaciated sites had stronger correlations with runoff over time than did non-glaciated sites due to the grinding of rock by moving ice (Gislason et al., 2009). However, the presence of glaciers had a much smaller effect on chemical weathering rates in that study.

An important relationship between physical and chemical weathering was proposed by Gilbert (1877) and developed by Carson and Kirby (1972) and Stallard and Edmond (1983), who differentiated mineral selectivity in terms of weathering-limited and transport-limited denudation regimes, where denudation refers to the total mass lost by the combination of chemical weathering and physical erosion. This concept is analogous to reaction-limited (also called interface-limited) and transport-limited weathering, used to describe controls on mineral
dissolution rates in the laboratory, but also applied to chemical weathering in field settings (Berner 1978; Kump et al., 2000).

In the weathering-limited denudation regime, physical removal of material by erosion is faster than the breakdown of material by weathering, therefore the most reactive phases will be available for chemical weathering. In this case, physical erosion removes regolith that still contains un-weathered phases. This regime is also sometimes referred to as kinetic-limited (e.g., West et al., 2005; Lebedeva et al., 2010) because chemical weathering fluxes are controlled by the kinetics of the mineral weathering reactions in addition to mineral solubility and the fluid saturation state (see section 5.04.7.4.1 Temperature). As such, reaction rates in the field can be as fast as those measured in the laboratory, particularly in settings with high flow rates, which prevent waters from becoming thermodynamically saturated with respect to the weathering minerals.

The oxidation of ferrous-containing biotite to oxybiotite with the release of interlayer K provides an example of weathering-limitation. This rapid weathering reaction is documented by high K fluxes in present day glacial watersheds in which large amounts of fresh rock are exposed by physical erosion (Anderson et al., 1997; Blum and Erel, 1997; Tranter, this volume). Such excess K is not observed in watersheds that are geomorphically older.

Under transport-limited weathering, sometimes also referred to as supply-limited weathering, the amount of fresh rock available to be weathered is limited. In this case, chemical weathering is faster than physical erosion and available minerals ultimately contribute to the solute load in proportion to their abundance in the bedrock. Weathering fluxes in this regime are not controlled by mineral reaction kinetics, but do reflect thermodynamic constraints. The build-up of weathering products often leads to chemical weathering reactions that occur near thermodynamic equilibrium. Indeed, this regime is sometimes referred to as a local-equilibrium regime (Lebedeva et al., 2010; Brantley and Lebedeva, 2011). Transport-limited weathering is common in geomorphically older settings. An example is the nearly complete destruction of aluminosilicates from old laterites and saprolites in which base cations are all effectively removed from the regolith.
Denudation regimes have recently been highlighted in the debate over the relative importance of climate versus tectonic controls on chemical weathering rates, with important implications for global climate models. Gabet and Mudd (2009) produced a theoretical model based on the concept that the relationship between physical erosion and chemical weathering should differ in landscapes where denudation is transport-limited (linear relationship) versus weathering-limited (power-law relationship) as originally put forward by West et al. (2005). This model reconciles apparently conflicting results of previous researchers that show either strong or weak tectonic (erosion) or climate (temperature) control on global chemical weathering rates. The model results of Gabet and Mudd (2009) demonstrated that during the early stages of orogeny, when denudation is transport-limited, an increase in physical erosion driven by uplift produces large increases in chemical weathering, but that as erosion rates continue to increase, the effect on chemical weathering rates diminishes. At very high erosion rates, denudation becomes weathering-limited such that material is eroded before it has a chance to chemically weather.

5.04.8. SUMMARY

This paper reviews the chemical, physical and hydrologic processes that control silicate mineral weathering at the earth’s surface. Silicate weathering rates are fluxes that describe mass transport across an interface over a given time interval. Quantitative rates of weathering are important in understanding reaction mechanisms and in addressing a number of economic and environmental issues.

Mass change, defined in terms of elements, isotopes or mineral abundances is determined from either solid or solute compositions. Solid state mass changes in a bulk regolith must be corrected for the mobility of all components as well as volume and density changes due to compaction and bioturbation. This correction is commonly done by normalizing reactive concentrations against an element or mineral considered to be resistant to chemical weathering. Weathering in solid materials is also characterized on microscopic levels based on weathering rind thickness and mass losses due to porosity and etch pit development.
The calculation of rates based on changes in solute species concentrations in soils, aquifers and watersheds requires partitioning the reactant between sources produced by primary mineral dissolution and sinks created by secondary mineral precipitation. Calculation of weathering rates based on solute transport requires knowing the nature and rate of fluid flow through soils, aquifers and watersheds.

The duration of weathering is very different depending on whether changes in solid or solute concentrations are measured. Solid state mass differences reflect weathering over geologic time scales while solute compositions reflect the residence time of the water. These mass losses or gains are normalized to surface area. Rates of reaction are directly proportional to the density of reactive sites on a silicate surface. Natural rates equate this density with the physical surface area of the weathering environment, generally defined on a geographic, volumetric or mineral-specific basis. Specific surface areas are either geometric estimates based on particle size dimensions or else based on BET gas sorption isotherms which include surface areas associated of microscopic roughness and internal porosity. The difference in the scales of these measurements produces major differences in surface-normalized mineral weathering rates.

The majority of rate studies are based on watershed solute fluxes normalized to catchment area and are equivalent to rates of chemical denudation. Previous efforts have tabulated these rates, which have proven valuable in evaluating the importance of a number of environmental controls on chemical weathering including precipitation, temperature, vegetation, tectonic setting, and rock type. The present chapter summarizes literature rate data for the weathering of several common silicate minerals based on geographic and specific surface areas. In the latter case, differences between geometric and BET-based surface areas are removed by normalizing the rates against an estimated time-dependent surface area roughness factor. Results confirm that a significant correlation exists between decreases in weathering rates with increases in weathering duration.

Factors affecting weathering rates can be categorized as either intrinsic or extrinsic to a specific silicate mineral. The primary intrinsic factors controlling weathering rates are mineral composition and structure. Reaction rates are also affected by compositional differences within
single mineral grains, such as zonations and exsolution features and by secondary surface coatings and leached layers.

Of the extrinsic factors influencing natural weathering rates, solute composition has the most direct impact. Solutions provide reactants that complex with and detach the oxygen-bonded metal species in the silicate structure. In addition, reaction rates depend on the thermodynamic saturation state of the dissolving phase. Unlike most experimental studies, natural weathering commonly involves long times and small solute/solid ratios, producing solutes close to thermodynamic saturation. This difference in saturation states explain, in part, why natural weathering rates are commonly orders magnitude slower than experimental rates and why the relative weatherability of minerals in the natural environment is often different from that predicted by experimental dissolution rates.

The origin of the term “weathering” implies that chemical weathering is related to climate. However, the exact nature of this relationship remains an area of significant controversy. Studies comparing weathering rates in soils and small catchments often find a significant climate effect while solute concentrations and fluxes originating from large river systems often fail to detect a climate signature. This discrepancy is related to the ability to isolate the effects of climate from other often codependent parameters which decrease as the scale of the weathering processes increases and may also reflect differences in denudation regime. An exponential relationship between reaction rate and temperature is observed in some weathering environments. Several studies have also documented linear increases in weathering with precipitation due to increases in wetted surface areas and thermodynamic reaction affinities.

As expected, the ratio of physical to chemical weathering is strongly scaled to differences in topography, but this is likely due to active tectonics in mountainous settings rather than due to the topography itself. An important relationship between physical weathering and chemical weathering is summarized in terms of weathering-limited and transport-limited weathering regimes. In addition to controlling the relative proportions of minerals available for weathering, physical erosion also has a profound effect on the physical development of the weathering environments. Regoliths can be viewed as aggrading, steady state or degrading
systems depending on whether their thickness increases, remains constant or decreases with time due to physical erosion.

Most weathering occurs within the “critical zone”: the region of the Earth extending from the vegetation canopy to fractured bedrock. Chemical weathering breaks down rocks to form soils, a process that literally forms the Critical Zone and makes life possible on our planet. Processes that alter the critical zone are recorded in the geochemistry of the regolith. As a result, chemical and mineralogical regolith profiles are invaluable for deciphering the physical, chemical, and biological history of the critical zone, identifying reaction mechanisms, and calculating weathering rates.

REFERENCES


Blackwelder, E., 1925. Exfoliation of a phase of a rock weathering. J. Geology 33, 625-635.


Chamberlin, T.C., 1899. An attempt to frame a working hypothesis of the cause of glacial periods on an atmospheric basis. *J. Geology* 7, 545-584.


### NOMENCLATURE

- **b**<sub>solid</sub> solid weathering gradient (m kg mole<sup>-1</sup>)
- **b**<sub>solute</sub> solute weathering gradient (m L mole<sup>-1</sup>)
- **c** concentration of weatherable component in solute (molar)
- **C**<sub>j,w</sub> final concentration of weatherable component j in regolith (moles m<sup>-3</sup>)
- **C**<sub>j,p</sub> initial concentration of weatherable component j in protolith (moles m<sup>-3</sup>)
- **C**<sub>i,w</sub> final concentration of inert component i in regolith (moles m<sup>-3</sup>)
- **C**<sub>i,p</sub> initial concentration of inert component i in protolith (moles m<sup>-3</sup>)
- **d** mineral grain diameter (m)
- **D** total denudation rate (m s<sup>-1</sup>)
- **D**<sub>j</sub> diffusion coefficient (m<sup>2</sup> s<sup>-1</sup>)
E  Physical erosion rate (m s⁻¹)
Eₐ  Activation energy (kJ mole⁻¹)
ΔG  Excess free energy of reaction (kJ mole⁻¹)
ΔH  Enthalpy of reaction (kJ mole⁻¹)
VH  Hydraulic gradient (m m⁻¹)
hₕ  Gravitational head (m m⁻¹)
hₚ  Pressure head (m m⁻¹)
IAP  Ionic activity product
Kₛ  Mineral solubility product
Kₘ  Hydraulic conductivity (m s⁻¹)
k  Intrinsic rate constant
ΔM  Change in mass due to weathering (moles)
mⱼ  Atomic wt. of component j (g)
P  Annual precipitation (m)
qₜ  Flux density of water (m s⁻¹)
Q  Solute flux (moles ha⁻¹ yr⁻¹)
Rₙsolid  Reaction rate based on solid concentrations (moles m⁻² s⁻¹)
Rₙsolute  Reaction rate based on solute concentrations (moles m⁻² s⁻¹)
R'  Gas constant (joules mole⁻¹ oK⁻¹)
S  Surface area (m²)
Sₛ  Specific surface area (m² g⁻¹)
Sᵥ  Volumetric surface area (m² m⁻³)
T  Temperature (°K)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>t</td>
<td>Duration of weathering (s)</td>
</tr>
<tr>
<td>$V_s$</td>
<td>Volume of solute</td>
</tr>
<tr>
<td>$V_m$</td>
<td>Molar volume (m$^3$)</td>
</tr>
<tr>
<td>W</td>
<td>Chemical weathering flux (m s$^{-1}$)</td>
</tr>
<tr>
<td>z</td>
<td>Distance (m)</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Stoichiometric coefficient</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Volumetric strain</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Porosity (m$^3$ m$^{-3}$)</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Surface roughness (m$^2$ m$^{-2}$)</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Solute weathering velocity (m s$^{-1}$)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Specific mineral density (m$^3$ g$^{-1}$)</td>
</tr>
<tr>
<td>$\rho_p$</td>
<td>Density of regolith (g cm$^3$)</td>
</tr>
<tr>
<td>$\rho_w$</td>
<td>Density of protolith (g cm$^3$)</td>
</tr>
<tr>
<td>$\tau_j$</td>
<td>Mass transfer coefficient</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Solid state weathering velocity (m s$^{-1}$)</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>Thermodynamic saturation state</td>
</tr>
</tbody>
</table>
Figure Captions

Figure 1. A schematic picture of the “weathering engine” at the Earth’s surface. As shown physical, chemical, and biological processes combine to control regolith in the Critical Zone. Climatic, anthropogenic, and tectonic forcings affect these processes; the sum total of weathering processes can then be read in changes in the atmosphere, hydrosphere, and pedosphere (after Anderson et al., 2004).

Figure 2. Distribution of sodium in pore waters and regolith formed in granitic sediments of the Santa Cruz marine terrace sequence (after White et al., 2008; 2009).

Figure 3. Schematic showing the relationships between solid state and solute weathering profiles gradients, rates and velocities (after White 2002; 2009). The soil surface is z₀. a) Mᵣ and Mₚ correspond to the solid regolith and protolith compositions. The parallel diagonal lines denote the progressive advance of the solid state weathering profile with z over geologic time. b) mₑ corresponds to the net solute component derived from weathering (Eqn. 3) and mₚ is the solute composition in equilibrium with the protolith. Over contemporary times, the solute profile does not advance with z.

Figure 4. Weathering indices for the Hawi basalt flow, Hawaii. Designations refer to specific indices tabulated in Table 1 (data from Chadwick et al., 2003).

Figure 5. Comparison of soil volume changes (€ in Equation 8) with elemental gains and losses (τ in Equation 9) in soils of the Santa Cruz chronosequence, California (after White et al., 2008). Values of unity are indicative of the protolith composition.

Figure 6. Volume (a) and elemental changes (b) in the Panola regolith, Georgia, USA. Volume changes are calculated separately assuming conservancy of Zr, Nb and Ti. Positive values of € (Equation 8) indicate dilation and negative values indicate compaction. Positive values of τᵣ (Equation 9) indicate elemental enrichment and negative values denote elemental mobilization and loss (after White et al., 2000).

Figure 7. Primary minerals lost (positive values) and secondary minerals produced (negative values) during weathering of the Panola regolith. Horizontal lines denote regolith horizons (after White et al., 2001).
Figure 8. Soil profiles depicting the characteristics of (a) immobile, (b) depletion, (c) depletion-enrichment, (d) addition and (e) biogenic end members as described in text. Plots show values of $\tau_j$ calculated assuming Ti or Zr are immobile plotted on the x axis, and depth on the y axis. All data derive from regolith developed on Rose Hill shale in the Susquehanna Shale Hills Observatory in central Pennsylvania USA (after Jin et al., 2010).

Figure 9. Progressive evolution of weathering profiles with time in a model system consisting albite in a matrix of quartz. The volume fraction of albite is plotted versus depth in the absence of physical erosion (Lebedeva et al., 2007).

Figure 10. Evolution of plagioclase weathering profiles in the Santa Cruz soil chronosequence for soils of increasing age. Data points are residual plagioclase concentrations as measured by XRD and normalized to the original sediment composition. Solid lines are best fits using a spread sheet profile calculator (White et al., 2008). The shaded areas enclose dashed lines representing forward and backward evolution of profiles with time based on fitted parameters for individual profiles (after White et al. 2008).

Figure 11. Plagioclase weathering profile in a 194 kyr old soil developed on a marine terrace deposit, Santa Cruz, California. Solid points are measured residual mineral plagioclase concentrations and solid line is the fitted profile based on Equation 35. The weathering gradient is defined by $b_s$. Dashed lines correspond to the projected position of the profiles at past and future soil ages based on the solid state weathering velocity. Plot is the application of the schematic profile defining solute weathering profiles in Figure 3b.

Figure 12. Albite depletion profiles plotted as $\tau_j$ (Equation 8) versus depth for a hypothetical profile describing albite weathering to kaolinite assuming simplified, diffusion-limited isovolumetric regolith (Lebedeva et al. 2009). The steady-state curves document depletion of albite as a function of depth, contoured for various rates of erosion, $E$ (expressed as length time$^{-1}$).
Figure 13. Relationship between (a) seasonal moisture content, expressed as percent hydrologic saturation, and (b) experimental hydraulic conductivities (Km in Equation 20) in the Riverbank soil, Merced California (after Stonestrom 1998).

Figure 14. Selected pore water concentrations as functions of depth in a deeply weathered regolith in the Luquillo Mountains of Puerto Rico Diagonal solid lines are linear fits to the weathering gradients used by Murphy et. al (1998) to calculate biotite weathering rates (Equation 22).

Figure 15. Pore water distribution for (a) Si and (b) Na in the SCT 5 soil of the Santa Cruz chronosequence. Also shown are residual plagioclase distributions (shaded areas). c) Volumetric distributions of Na and Si in (c) correspond to mass losses ΔMsolute in Figure 3a and Equation 3. The slope of the approximate linear solute gradients defines bsolute. The weathering velocity is equivalent to the hydraulic flux qs.

Figure 16. Hydrologic properties of a sandy silicate aquifer in Northern Wisconsin. (a) hydrologic conductivity’s, (b) Ground water potentials and (c) ground water residence times (after Kenoyer and Bowser, 1992).

Figure 17. Cross sections showing the vertical distribution of Si and Ca in ground water in the North Wisconsin aquifer (after Bullen et al., 1996).

Figure 18. (A) Dissolved Si and Mg in discharge from the Panola catchment, Georgia, USA. Dashed lines encompass calculated hillslope, groundwater and shallow soil (organic) inputs (after Hooper et al., 1990).

Figure 19. Surface area parameters for minerals as functions of age in Merced chronosequence (after White et al, 1996). (a) Surface area of primary silicate minerals. (b) Surface roughness of silicate minerals as functions of the duration of experimental and natural weathering. Diagonal line corresponds to the fit of Equation 25. Data summarized from White and Brantley (2003).

Figure 20. Relationship between weathering rate and reaction time for (a) K-feldspar and (b) plagioclase. Field weathering rates are summarized from White and Blum (1995) and White and Brantley (2005) with additional new data (Föllmi et al., 2009; Buss et al.,

Figure 21. Comparison of present day and long term plagioclase weathering based on the respective ratios of weathering gradients and velocities for Santa Cruz marine terraces of different ages (Equations 3 and 4). Representative data contained in Figures 11 and 15. Equal rates are represented by the dashed line as unity (after White et al., 2009).

Figure 22. Mica weathering in a saprolite profile from central Georgia USA. (a) Changes in mole % K and Al/Si mole ratios in coexisting biotite and muscovite. (b) SEM backscatter photomicrograph of residual biotite grains at 2.8 m. Bright layers in the left grain are unaltered biotite and gray areas are kaolinite replacement. Right grain is completely kaolinitized biotite with surficial box work structure (after White et al., 2002).

Figure 23. Primary silicate weathering in the Panola regolith (a) Back-scatter SEM micrograph of weathered granite at a depth 7.5 m. The center grain is a plagioclase phenocryst almost completely replaced by kaolinite (dark region). Minor residual plagioclase remains on outside rims of grain. Saturation states of soil pore water (+) and groundwater (●) relative to (b) plagioclase (albite) and (c) K-feldspar (after White et al., 2001).

Figure 24. Effect of a factor of 5 increase or decrease in the kaolinite precipitation rate (relative to best-fit value) on mineral profiles in the SCT soil in the Santa Cruz chronosequence a) kaolinite profile; b) albite; c) K-feldspar, also shown for reference is the weathering profile in the absence of kaolinite precipitation. Albite and K-spar rate constants are from Table 4 (after Maher et al., 2009).

Figure 25. Coupling of weathering rates and hyrologic flow in the weathering of low permeability rocks. a) Schematic showing weathering zones as coupled functions of increasing weathering intensity and permeability denoted by increases in hydraulic conductivities. \( q_p \) is primary permeability of bedrock and \( q_s \) is secondary permeability, or permeability of saprolite, reflecting mass depletion due to weathering. In this schematic, the arrow, signifying progressive increases in weathering, can be considered either to represent duration of weathering, or decreasing soil depth (after White et al., 2001). b) Percent of plagioclase and K-feldspar reacted as a function of the ratio of secondary to primary
fluxes ($q_s/q_p$) in the Panola Granite, where $q_p$ is assumed to be equivalent to the steady-state propagation rate of the weathering front as determined from cosmogenic isotopes (Pavich et al., 1995) and $q_s$ is a fitted parameter. The vertical dashed line is the approximate flux ratio required to completely weather plagioclase while preserving K-feldspar (Figure 23a).

Figure 26. Calcite distributions in the Panola Granite a) cathodoluminescent photomicrograph of Panola Granite thin section showing disseminated calcite internally distributed in a K-feldspar grain, b) Comparison of weathering profiles for CaO, dominated by plagioclase and trace amounts of calcite. The advancement of the calcite suggests that it may create sufficient secondary porosity to initiate plagioclase but not K-feldspar weathering (Figure 25b).

Figure 27. Simplified diagram of the spheroidal weathering profile in the Rio Icacos watershed. The quartz diorite bedrock is rounded into corestones, which fracture concentrically forming rindlets. A sequence of rindlets comprises a rindlet zone. Highly weathered rindlets are hand friable saprock (also known as ‘protosaprolite’), which eventually degrade to form saprolite (after Buss et al., 2008).

Figure 28. The formation of sequential spheroidal fractures in the Rio Icacos quartz diorite modeled as a function of Fe(II) oxidation biotite (solid line). Steps in the model line indicate representing the formation of rindlet-defining macro-cracks. The measured Fe(II) gradient (solid squares) across the rindlet zone indicates that, similar to the numerical model, biotite oxidation begins near the corestone with a large loss of Fe(II), which tapers off near the saprolite (after Buss et al., 2008).

Figure 29. Comparison between measured and calculated feldspar weathering profiles in SCT 5 Santa Cruz soil. The solid lines are the best least squares fits to the measured plagioclase profiles (●) using a fluid flux of $q_h = 0.058 \text{ m yr}^{-1}$ and a weathering rate constant of $k_r = 4.8 \times 10^{-16} \text{ moles m}^{-2} \text{ s}^{-1}$). Dashed lines in each plot show the effects on calculated profiles by increasing and decreasing $q_h$, and $k_r$). Open circles indicate data not fitted in calculation (after White et al, 2008).
Figure 30. Arrhenius relationship between temperature and rates for basalt weathering. a) Rates based on porosity increases in plagioclase from Hawaiian basalt flows (Dorn and Brady, 1995). b) Rates based on solute bicarbonate fluxes from a global distribution of watersheds underlain by basalt (Dessert et al., 2001).

Figure 31. Relationship between Si fluxes and runoff from watersheds draining (a) granitic and (b) basaltic rocks (after Bluth and Kump, 1994).

Figure 32. Three-dimensional surface representing the optimized fit of watershed Si fluxes to Equation 32 as functions of precipitation and temperature (after White and Blum, 1995).