

Solute geochemical mass-balances and mineral weathering rates in small watersheds: Methodology, recent advances, and future directions

Michael A. Velbel ^{a,*}, Jason R. Price ^b

^a Department of Geological Sciences, 206 Natural Science Building, Michigan State University, East Lansing, MI 48824-1115, USA

^b Department of Earth Sciences, Millersville University, Millersville, P.O. Box 1002, PA 17551-0302, USA

Available online 23 March 2007

Abstract

Solute-based geochemical mass balance methods are commonly used in small-watershed studies to estimate rates of a variety of geochemical processes at the Earth's surface, including primary-mineral weathering and soil formation, and the quantitative contribution of these elemental transfer processes to cation budgets, nutrient cycling, and landscape susceptibility to acid deposition. Weathering rates of individual minerals in watershed mass-balance studies are determined by solving a system of simultaneous linear geochemical mass-balance equations with constant (stoichiometric) coefficients. These equations relate the measured net fluxes to the (known) stoichiometries and (unknown) rates of weathering reactions for multiple minerals in the weathering profiles. Solving the system of equations requires petrologic, mineralogic, hydrologic, botanical, and aqueous geochemical data. The number of mineral-weathering rates that can be determined is limited by the number of elements for which solute mass-balance equations can be written. In addition to calculating mineral weathering rates, elemental transfer into or out of the biomass may also be calculated. Elemental uptake by aggrading forest vegetation can act as an intrawatershed sink for at least some mineral-derived cations, producing mineral weathering rates higher than would be estimated from solute fluxes alone; similarly, element release from decaying forest biomass can result in higher solute fluxes than are produced by weathering alone. The mathematics of, significant contributions from, role of biomass in, and recent advances in, watershed geochemical mass-balance methods are discussed using examples from the Appalachian headwaters watersheds of the Coweeta Hydrologic Laboratory in the southern Blue Ridge Physiographic Province of North Carolina, USA.

© 2007 Elsevier Ltd. All rights reserved.

1. Introduction

The ability to quantify rates of mineral weathering, in particular silicate mineral weathering, is

essential not only for basic understanding of chemical weathering processes, soil formation and geochemical cycling, but is also of practical importance (Brantley, 2003; White, 2003). Silicate mineral weathering is a natural mechanism by which atmospheric CO₂ is consumed over geologic time, and therefore has a significant impact on the global C cycle and climate change (e.g., Berner

* Corresponding author.

E-mail address: velbel@msu.edu (M.A. Velbel).

et al., 1983; Berner, 1995; Berner and Kothavala, 2001). In ecosystems, the chemical weathering of silicate rocks results in the release of plant macronutrients to soils such as Mg, Ca, K and PO_4 , as well as micronutrients such as Fe, Mn and B (e.g., White and Brantley, 1995; Marschner, 1995). Silicate mineral weathering is also the only process capable of contributing to natural neutralization of landscape acidification resulting from atmospheric inputs of H and S in landscapes and regoliths lacking carbonate minerals (e.g., Katz et al., 1985; Bricker, 1986; April et al., 1986; Bricker and Rice, 1989; Likens and Bormann, 1995).

One method of calculating weathering rates of individual primary and secondary minerals in natural systems uses geochemical mass-balance methods (input–output budgeting) in small watersheds (e.g., Garrels, 1967; Garrels and Mackenzie, 1967; Cleaves et al., 1970, 1974; Clayton, 1979, 1986; Bricker et al., 1983, 2003; Pačes, 1983, 1986; Katz et al., 1985; Katz, 1989; Velbel, 1985a, 1986, 1992, 1995; Drever and Hurcomb, 1986; Taylor and Velbel, 1991; Finley and Drever, 1997; Furman et al., 1998; Bowser and Jones, 2002 and references therein; Price et al., 2005a). Geochemical mass-balance methods are considered the most reliable means for making quantitative determinations of elemental transfers at the Earth's surface environment (Clayton, 1979; Bricker et al., 2003), and perhaps the most accurate means of defining weathering reactions in natural systems (Bricker et al., 2003).

The purpose of this paper is to review watershed geochemical mass-balance methods conceptually and mathematically as presented in the recent literature, and to propose future considerations for how watershed geochemical mass-balance might be used. This paper only addresses solute-based mass-balance techniques using present-day (short-term) stream solute concentrations in order to calculate mineral weathering rates. Other techniques for determining long-term (multi-millennia) weathering rates and elemental flux losses from regolith using solid phase data have been developed (e.g., April et al., 1986; Brimhall and Dietrich, 1987; White, 2003; Riebe et al., 2003, 2004a,b), but will not be discussed here. The applications reviewed here are confined to small, low-order headwater watersheds; larger-scale watersheds (e.g., river basins) and/or larger drainage basins with complex mosaics of different ecosystems or land-use regimes are beyond the scope of this review.

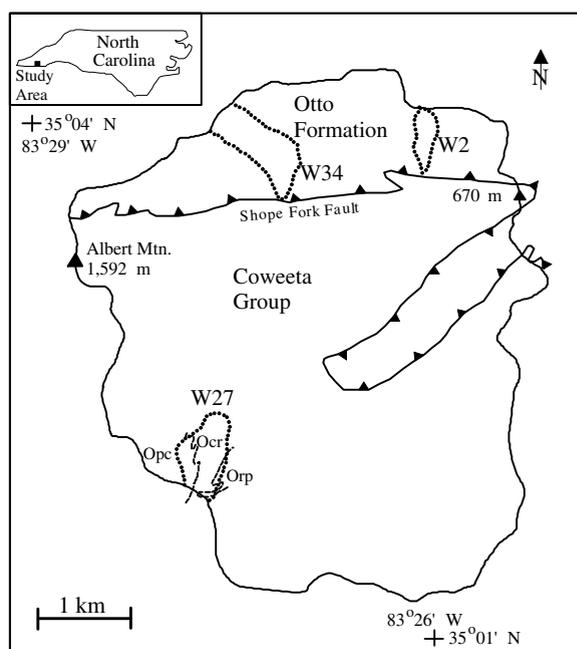


Fig. 1. Map of Coweeta Hydrologic Laboratory showing example watersheds and bedrock geology. Bedrock units for watershed 27 (W27) are: Opc = Persimmon Creek Gneiss, Ocr = Coleman River Formation, and Orp = Ridgepole Mountain Formation.

Illustrative examples of solute-based mass-balance techniques are drawn from the literature (e.g., Velbel, 1985a; Taylor and Velbel, 1991; Price et al., 2005a) on watersheds of the US Forest Service Coweeta Hydrologic Laboratory, located in western North Carolina, USA (Fig. 1). This paper uses Coweeta to illustrate the mathematics of, significant contributions from, role of biomass in, and recent advances in, watershed geochemical mass-balance methods.

2. Study area

The Coweeta Hydrologic Laboratory is located in the southeastern Blue Ridge Physiographic Province of western North Carolina (Fig. 1). The Coweeta Basin is quite rugged (average slope of approximately 45%/23°) and is underlain by the amphibolite facies metasediments of the Coweeta Group (mid-Ordovician; Hatcher, 1988; Miller et al., 2000) and the Otto Formation (Upper Precambrian; Hatcher, 1980, 1988). Coweeta Group and Otto Formation rocks are juxtaposed as a result of thrusting of the premetamorphic Shope Fork Fault (Hatcher, 1988; Fig. 1).

Saprolite mantles the landscape at Coweeta, although bedrock crops out locally, especially near

ridge crests. The term “saprolite” was proposed by Becker (1895) in his study of Au in the Appalachians (where saprolite is common; Mills et al., 1987) “as a general name for thoroughly decomposed, earthy, but untransported rock”. Over the years the definition has come to mean a residual regolith (Taylor and Eggleton, 2001) developed isovolumetrically on crystalline rocks, in which some or all of the primary minerals have been extensively transformed to weathering products. Rock textures, fabrics, and structures are preserved in the saprolite because the weathering products are usually pseudomorphous after the parent minerals (e.g., Velbel, 1990; Nahon, 1991; Delvigne, 1998). Isovolumetric preservation of parent-rock textures permits positive identification of the parent material, and provides a framework against which the spatial redistribution of the chemical constituents of parent- and secondary-minerals can be measured (Gardner et al., 1978, 1981; Gardner, 1980; Velbel, 1990; Price and Velbel, 2003; Patino et al., 2003). The average weathering profile (saprolite and soil) at Coweeta is approximately 6 m thick (Berry, 1976; Yeakley et al., 1998), with maximum thickness of 18 m (Berry, 1976; Ciampone, 1995). Total topographic relief in the Coweeta basin is approximately 1 km (Fig. 1). The narrow range of weathering-profile dimensions (0–18 m) on a landscape with steep slopes and an elevation range of nearly a kilometer suggests that the saprolite at Coweeta is not an ancient, relict, deep weathering profile but is instead related to and forming on the present landscape (Velbel, 1985a). Soils (mostly Ultisols and Inceptisols) constitute the uppermost 30 cm of the profile (Velbel, 1985a, 1988).

Climate varies appreciably from west to east across the Coweeta Basin. Mean annual precipitation varies from 250 cm on the upper slopes along its western boundary to 170 cm at the lower elevations to the east (Swank and Douglass, 1977). Stream specific discharge from the areas of high precipitation is more than double that from areas of low precipitation (Velbel, 1985a; Grantham and Velbel, 1988). Precipitation varies throughout the year, with autumn months being driest and the maximum precipitation in late winter and early spring with only a minor amount falling as snow (Swank and Douglass, 1977; Swift et al., 1988). Overland flow on a well-forested watershed is essentially non-existent (Swank and Douglass, 1977), as rain almost always infiltrates into the forest floor as fast as it falls (Helvey and Patric, 1988). Velbel (1985b) dem-

onstrated that the streams at Coweeta are samples of subsurface water which have undergone no significant change after leaving the saprolite to enter the streams, except re-equilibration with atmospheric gases which affects pH. Coweeta has a temperate climate with a mean annual temperature of 12.6 °C (Swift et al., 1988).

An extensive ground water aquifer has not been shown to exist at Coweeta (Hewlett, 1961). Instead, nearly all stream water passes through the soil and saprolite mantle, with continuous base flow to perennial streams resulting from water draining from pore space in the unsaturated zone (Hewlett, 1961; Hewlett and Hibbert, 1963; Velbel, 1985a,b).

3. Methods and background

3.1. Mathematics of watershed geochemical mass balance

Watershed geochemical mass balance employs a “balance sheet” approach, in which a system of simultaneous linear equations with constant coefficients represents the steady-state input–output behavior of the modeled systems (Velbel, 1985a; Taylor and Velbel, 1991; Bricker et al., 2003). Elemental inputs include precipitation, biomass decomposition (for degrading biomass), mineral weathering reactions, and in some instances depletion of the soil cation-exchange complex, while elemental outputs include evapotranspiration, botanical uptakes (for aggrading biomass), genesis of clay minerals and other weathering products, and stream discharge (Fig. 2). Inputs and outputs from agricultural systems also require consideration in studies of larger watersheds, but the examples reviewed here are predominantly small forested headwater watersheds with limited ecosystem modification by anthropogenic land-use practices. Methods for quantifying precipitation inputs and stream

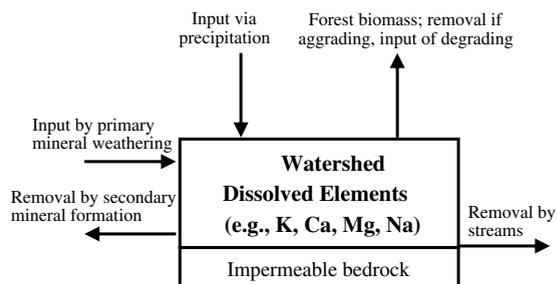


Fig. 2. Conceptual diagram of watershed geochemical mass-balance (after Velbel, 1985a, 1986).

outputs are discussed by Creasey et al. (1986), Swank and Waide (1988), and Likens and Bormann (1995). A fundamental requirement of watersheds to which mass-balance methods are being applied is that they are hydrologically “tight” (e.g., Velbel, 1985a,b; Creasey et al., 1986); that is, there is no ground water storage, depletion, or leakage to a regional aquifer. This assumption is generally valid for watersheds developed on crystalline silicate bedrock. At Coweeta, Cl^- is approximately in balance in all watersheds (Swank and Waide, 1988, their table 4.11), and, hence, loss of water to ground water is not of concern (Swank and Douglass, 1977).

Based on a whole-water mass-balance (input–output budget) for a watershed, simple mathematical methods enable quantification of the contributions of individual mineral phases and other (e.g., biological) materials to the overall watershed mass balance. The mathematical treatment of geochemical mass balances in small watersheds is conceptually identical to the mathematics of single reservoirs in global geochemical cycles (Velbel, 1986; Taylor and Velbel, 1991). Mass-balance methods do not require thermodynamic constraints (Bricker et al., 2003), but rather rely solely on field and laboratory measurements.

Following Plummer and Back (1980), Velbel (1986) (see also Taylor and Velbel, 1991) derives the following mass-balance expression for a system assumed to be in steady-state:

$$\sum_{j=1}^{\phi} \alpha_j \beta_{c,j} = \Delta m_c \quad c = 1, \dots, n$$

where, ϕ is number of unknowns; the number of weathering phases j ; α is the chemical weathering rate of phase j (units of a flux [$\text{mol ha}^{-1} \text{a}^{-1}$]). Note: Units of concentration (e.g., $\mu\text{mol L}^{-1}$) may also be used, in which case this variable is termed a “mass-transfer coefficient” (or MTC; Bowser and Jones, 2002). β is the stoichiometric coefficient of species c in phase j ; Δm_c is the total change in mass of species c (units of a flux [$\text{mol ha}^{-1} \text{a}^{-1}$]; if α is treated as a MTC, then units of concentration are used); and n is the number of mass-balance equations.

The solution of n equations in $\phi = n$ unknowns is mathematically unique, regardless of the stoichiometric coefficients used, and/or whether some additional process in addition to those described by the stoichiometric coefficients has been ignored (Taylor and Velbel, 1991).

Bowser and Jones (2002) use the same equation; following earlier applications (Plummer and Back, 1980) they define Δm_c as differences in concentration between output and input, and calculate mass transfer coefficients (MTC; units of concentrations [e.g., $\mu\text{mol L}^{-1}$]). Following Cleaves et al. (1970), Velbel (1985a, 1986) adapted the term Δm_c as a flux with dimensions of moles per unit area of watershed per unit time (typically $\text{mol ha}^{-1} \text{a}^{-1}$). This introduces time into the equations and into (α) , allowing calculations of rates and comparison of mineral weathering rates in watersheds with geochemical kinetics of similar reactions in other settings. Elemental flux out of a watershed is easily calculated by multiplying stream discharge by the elemental concentration of the stream water, and dividing by watershed area (e.g., Creasey et al., 1986); elemental flux into a watershed is similarly calculated from precipitation amounts and chemistry (Swift et al., 1988).

In practice, the above mathematics is actually relatively straightforward, and is demonstrated using an example adapted from Taylor and Velbel (1991). They used optical petrography, scanning electron microscopy (SEM), and X-ray diffraction (XRD) to identify the minerals involved in weathering, and electron microprobe phase analyses (EMPA) to determine the composition of these minerals. Although simplified or idealized (“textbook”) compositions of minerals have been used with some success in watershed mass-balance calculations, the use of watershed-specific mineral chemistry provides a closer approximation to the real geochemical behavior (Bowser and Jones, 2002; Bricker et al., 2003). For Coweeta Watershed 2 (W2; Fig. 1) Taylor and Velbel (1991) identified plagioclase feldspar (Velbel, 1983), almandine garnet (Velbel, 1984), and biotite as being the primary minerals weathering, and biotite transforming to secondary vermiculite with conservation of the silicate sheet (e.g., Newman, 1987). The chemical formula (and hence stoichiometric coefficients [β] for each element [species c]) for each of these three (ϕ) primary minerals (j) involved in weathering are provided in Table 1.

The transformation of biotite to vermiculite deserves special attention. Because vermiculite is a direct transformational product of biotite (e.g., Banfield and Eggleton, 1988), mathematical representation may reflect this “coupling” (the strengths and weaknesses of primary and secondary mineral coupling are discussed in detail below). Table 1 contains the stoichiometric difference in base cations between biotite and vermiculite, with elements taken

Table 1

Mineral composition data used for mass-balance calculations of primary mineral weathering rates in Watershed 2 at Coweeta Hydrologic Laboratory (Fig. 1; after Taylor and Velbel, 1991)

Mineral	Formula
Plagioclase feldspar	$\text{Na}_{0.68}\text{Ca}_{0.32}\text{Al}_{1.32}\text{Si}_{2.68}\text{O}_8$
Almandine garnet	$\text{Ca}_{0.2}\text{Mg}_{0.5}\text{Mn}_{0.2}\text{Fe}_{2.1}\text{Al}_2\text{Si}_3\text{O}_{12}$
Biotite	$\text{K}_{0.85}\text{Na}_{0.02}(\text{Mg}_{1.2}\text{Fe}_{1.3}\text{Al}_{0.45})(\text{Al}_{1.2}\text{Si}_{2.8})\text{O}_{10}(\text{OH})_2$
Vermiculite	$\text{K}_{0.25}\text{Na}_{0.06}\text{Ca}_{0.016}(\text{Mg}_{1.1}\text{Fe}_{1.6}\text{Al}_{0.45})(\text{Al}_{1.2}\text{Si}_{2.8})\text{O}_{10}(\text{OH})_2$
Stoichiometric difference of base cations between biotite and vermiculite reflecting conservation of the mica silicate sheet	$-0.016\text{Ca}, -0.04\text{Na}, +0.6\text{K}, +0.1\text{Mg}$

up by the vermiculite having a negative sign, and elements being lost from biotite during vermiculite formation having a positive sign. The differences in base cations between reactants and products serve as the stoichiometric coefficients $[\beta]$ for the weathering of biotite (to vermiculite) at Coweeta.

The values of the Δm_c terms, the fluxes of each element (species c) in the stream water draining the watershed (after subtraction of precipitation inputs), are reported in Table 2 (Price et al., 2005a). Sampling and analytical procedures for major solutes in the weekly samples, hydrologic (precipitation and discharge, for inputs and outputs, respectively) data, and the determination of solute fluxes from the combined chemical and hydrologic data, are explained in detail by Swank and Waide (1988). With the data from Table 1, a set of matrices can be constructed (Fig. 3).

The large matrix on the left of Fig. 3 is a matrix of the stoichiometric coefficients of elemental release

or uptake (β), the column vector immediately to the right of the coefficient matrix contains the unknown primary mineral weathering rates (units of $\text{mol ha}^{-1} \text{a}^{-1}$), and the column vector on the right of the expression contains the solute fluxes in the stream water after subtraction of precipitation inputs (also units of $\text{mol ha}^{-1} \text{a}^{-1}$; Table 2). Calculation of mineral weathering rates/MTCs using watershed mass-balance methods is easily performed by matrix inversion using any standard linear algebra matrix-solving method or software. The solution to the matrix expression shown in Fig. 3 is contained in Table 3. Notice the sign convention being used; by keeping all of the elemental stoichiometries (β) for plagioclase and garnet positive (reflecting the loss of elements due to mineral destruction), and the total change in mass of species c (Δm_c ; or the elemental flux in the stream water) positive, phases being destroyed during weathering will have positive weathering rates. Had secondary minerals been included in this calculation, rates of any phases being formed would have opposite (in this case, negative) values. Alternative sign conventions result in the same numerical values, with opposite signs for the calculated results.

Table 2

Elemental solute flux data for the Coweeta W2 stream water following subtraction of precipitation inputs (after Swank and Waide, 1988; Taylor and Velbel, 1991; Price et al., 2005a)

Element (c)	Flux (Δm_c ; $\text{mol ha}^{-1} \text{a}^{-1}$)
Mg	94.2
K	74.2
Na	359

$$\begin{array}{c}
 \text{Mg} \\
 \text{K} \\
 \text{Na}
 \end{array}
 \begin{bmatrix}
 \text{Plag} & \text{Garn} & \text{Biot} \\
 0 & 0.5 & 0.1 \\
 0 & 0 & 0.6 \\
 0.68 & 0 & -0.04
 \end{bmatrix}
 \begin{bmatrix}
 \alpha_{\text{Plag}} \\
 \alpha_{\text{Garn}} \\
 \alpha_{\text{Biot}}
 \end{bmatrix}
 =
 \begin{bmatrix}
 94.2 \\
 74.2 \\
 359
 \end{bmatrix}$$

Fig. 3. Coefficient matrix for Coweeta W2 (after Taylor and Velbel, 1991). Plag = plagioclase, Biot = biotite, and Garn = almandine garnet.

3.2. Historic background and significant contributions to watershed geochemical mass-balance techniques

This section reviews the general development of the watershed solute mass-balance approach, but is not intended to cover every different aspect and example of its implementation.

Table 3

Mineral weathering rates for the matrix equation in Fig. 3 (after Taylor and Velbel, 1991)

Mineral	Weathering rate ($\text{mol ha}^{-1} \text{a}^{-1}$)
Plagioclase feldspar	535
Almandine garnet	164
Biotite	124

All methods for calculating rates of mineral weathering using mass-balance calculations are ultimately based on the method first presented by Garrels and Mackenzie (1967). These authors used previously published spring water composition data from Feth et al. (1964) for the Sierra Nevada of California and Nevada, USA. Following subtraction of precipitation cation and anion inputs from the spring water, Garrels and Mackenzie (1967) explained the chemistry of the spring water as reflecting silicate mineral weathering when CO₂-charged precipitation interacted with the granitic bedrock in a closed system. They demonstrated that dissolved silica came primarily from the incongruent dissolution of silicate minerals (e.g., plagioclase and biotite) rather than from the congruent dissolution of quartz. The calculations of Garrels and Mackenzie (1967) relied on solute concentrations in spring waters, rather than fluxes, yielding MTCs for mineral weathering.

The next significant advancements in watershed geochemical mass-balance methods were introduced by Cleaves et al. (1970) for the Pond Branch watershed (MD, USA). Their contribution was two-fold. First, they utilized stream discharge measurements and watershed area, allowing for calculation of elemental fluxes from the watershed (units of kg acre⁻¹ a⁻¹ for their study; units of kg ha⁻¹ a⁻¹ or mol ha⁻¹ a⁻¹ have since become the more widely used units) and thereby introducing time and rates into solute mass-balance. The second contribution by Cleaves et al. (1970) was their explicit introduction of biomass into the solute mass-balances. They assumed that Mg, Na and SiO₂ were in dynamic equilibrium with biomass. By doing so they determined that their weathering reactions produced an excess of K, Ca and SO₄ over the amounts actually observed in the stream output. From this, they inferred greater uptake of these elements by biomass than the amount returned to the watershed by decay of organic matter. Therefore, the assumption of biomass being in steady-state was demonstrated not to apply to the Pond Branch watershed (Cleaves et al., 1970).

Velbel (1985a) explicitly incorporated biomass into the formalization of watershed geochemical mass-balance methods. In realizing that biomass cannot be assumed to be in steady-state (e.g., Cleaves et al., 1970), Velbel (1985a) calculated a biomass stoichiometry for the watersheds of Coweeta by converting published Coweeta biomass net primary production values (i.e., Day and Monk,

1977; Boring et al., 1981) for the base cations used in his mass-balance to molar proportions. This is similar to a related approach used by Bowser and Jones (2002), involving the use of a “fictive phase” (see below) with stoichiometric coefficients in this case representing the relative proportions of major-cation uptake by the aggrading Coweeta biomass. The Coweeta biomass term generated by Velbel (1985a) was Mg_{0.056}Ca_{0.144}Na_{0.008}K_{0.150}. When the biomass stoichiometry is entered into the matrix of coefficients as positive values, an aggrading biomass rate/MTC will be a negative value, and a degrading biomass rate/MTC will be a positive value. A biomass truly in steady-state will yield a biomass rate/MTC of near zero. The biomass rate of nutrient uptake for W2 based on the matrix expression in Fig. 4 is -1232 mol ha⁻¹ a⁻¹ (Table 4). The negative biomass value reflects nutrient uptake by an aggrading biomass. Velbel (1986) presented the mathematical formalization of geochemical mass-balance calculations outlined above. Based on this formalization, Taylor and Velbel (1991) demonstrated that for Coweeta watersheds,

$$\begin{array}{c} \text{Ca} \\ \text{Mg} \\ \text{K} \\ \text{Na} \end{array} \begin{bmatrix} \text{Plag} & \text{Garn} & \text{Biot} & \text{Biom} \\ 0.32 & 0.2 & -0.016 & 0.144 \\ 0 & 0.5 & 0.1 & 0.056 \\ 0 & 0 & 0.6 & 0.150 \\ 0.68 & 0 & -0.04 & 0.008 \end{bmatrix} \begin{bmatrix} \alpha_{\text{Plag}} \\ \alpha_{\text{Garn}} \\ \alpha_{\text{Biot}} \\ \alpha_{\text{Biom}} \end{bmatrix} = \begin{bmatrix} 45.4 \\ 94.2 \\ 74.2 \\ 359 \end{bmatrix}$$

Fig. 4. Matrix expression for W2 with inclusion of a biomass term (Biom) (after Taylor and Velbel, 1991). Plag = plagioclase, Garn = almandine garnet, and Biot = biotite.

Table 4

Comparison of mineral weathering rates for Coweeta W2 calculated with and without inclusion of a biomass term in the calculations (after Taylor and Velbel, 1991)

Mineral	Weathering rate (mol ha ⁻¹ a ⁻¹) with biomass term	Weathering rate (mol ha ⁻¹ a ⁻¹) without biomass term (Table 3)	Ratio of rates with biomass rate to without biomass rate
Plagioclase feldspar	568	535	1.1
Almandine garnet	240	164	1.5
Biotite	432	124	3.5
Biomass	-1232	-	-

neglecting the biomass term in watershed mass-balance calculations (Fig. 3) can cause mineral weathering rates to be underestimated of by up to a factor of almost 4 (Table 4) relative to rates calculated to include biotic influence (Fig. 4). Velbel (1995) extended this approach to other Appalachian watersheds.

Recently, Bowser and Jones (2002) and Bricker et al. (2003) investigated a variety of influences on the calculated mineral weathering MTCs using watershed mass-balance techniques. These included: (1) The influence of mineral composition(s); (2) Cases when the number of mineral phases exceeds the number of solutes (i.e., the number of unknowns exceeds the number of equations); and (3) The role of cation exchange. The geochemical reasonability of mineral weathering rates were often constrained by the thermodynamic stability of various mineral phases under near-surface weathering conditions. With respect to mineral compositions, Bowser and Jones (2002) and Bricker et al. (2003) found that the mass balance results are particularly sensitive to the compositions of plagioclase, dioctahedral smectite, and a few primary ferromagnesian minerals. For cases where the number of mineral phases exceeded the number of solutes, Bowser and Jones (2002) and Bricker et al. (2003) introduced the idea of the “fictive phase” in order to reduce the number of unknowns. These authors define a fictive phase as a proportional composition of two or more structurally similar minerals that may be treated as one phase if the dissolution or precipitation rates of the constituent minerals are always in the same proportion to one another; the biotite–muscovite relationship invoked by Velbel (1985a) and described below is an example of this approach. Bowser and Jones (2002) have utilized the fictive phases biotite/chlorite, pyroxene/amphibole, and road salt in watershed mass balance studies. Bowser and Jones (2002) found that cation exchange was only a concern for watershed mass-balance calculation of weathering rates when pre-existing waters are displaced by solutions of different composition.

Price et al. (2005a) included rare earth elements (REE) in their watershed mass-balance calculations, allowing for construction of a larger number of equations. A larger number of equations permit determination of weathering rates for a larger number of phases. Price et al. (2005a) established criteria to define geochemically reasonable ranges of calculated mineral weathering rates determined from stream flux data that included the REE. For the

watersheds investigated, the calculated mineral weathering rates were all well within the established ranges of geochemical reasonability.

3.3. Overcoming more unknowns than equations

Because mass-balance methods rely on solving systems of linear equations, there must be as many equations as unknowns. A fundamental limitation of watershed mass-balance calculations (e.g., Finley and Drever, 1997; Bowser and Jones, 2002; Bricker et al., 2003) is that complex natural systems may involve more unknowns (the rates of weathering of individual primary minerals and/or the rates of formation of secondary minerals) than equations (e.g., the number of elements for which stream solute data are available). Previous researchers using watershed mass balance methods have used a variety of approaches in attempting to overcome the limitation of having more unknowns than equations. These can be broadly divided into (1) invoking simplifying assumptions to reduce the number of unknowns requiring solution, and (2) increasing the number of equations available to increase the number of unknowns that can be determined by solving the system of equations.

3.3.1. Assumptions to reduce the number of unknowns

One commonly used way to eliminate an unknown is to not include a biomass term (e.g., Afifi and Bricker, 1983; Bowser and Jones, 2002; Bricker et al., 2003). This can be done in such a way as to provide additional insight into at least limiting conditions relating to the role of biomass (e.g., Cleaves et al., 1970). Excluding biomass in watershed mass balance is only valid if the biomass is in steady state during the period of sampling; that is, uptake by elements during the growth of new vegetation is exactly balanced by the release of elements from death and decay of old vegetation, and the biomass is neither a sink nor source of elements in the ecosystem (e.g., Taylor and Velbel, 1991; Likens and Bormann, 1995; Velbel, 1995; Drever, 1997; Bricker et al., 2003). However, in forested watersheds the biomass is rarely in a steady state (Taylor and Velbel, 1991; Likens and Bormann, 1995; Velbel, 1995; Drever, 1997). If a pseudo-stoichiometric expression for biomass can be constructed (in other words, if a compositionally relevant “fictive phase” is introduced for biomass), the sign and magnitude of biomass change can be calculated by solving for

biomass change as an unknown (Velbel, 1985a, 1995; Taylor and Velbel, 1991; Fig. 4; Table 4). Alternatively, direct measurements of biomass composition and aggradation might allow biomass to be treated as a known flux in the overall solute mass balance, rather than as an unknown (e.g., Moulton et al., 2000). Each watershed should be evaluated to determine the role of biomass and how it should be treated in light of the availability of site-specific data (Bricker et al., 2003).

Combining multiple minerals into a single unknown is an approach that has been employed in a number of ways in solute mass-balance studies of weathering rates. For the Coweeta W2 example above (Taylor and Velbel, 1991) weathering rates are solved for three minerals (ϕ), and three elemental stream fluxes (Δm_c), permitting a solution to the system of linear equations. However, if there were another phase involved in weathering, and stream water fluxes for additional elements were unavailable, no mathematical solution is possible without invoking simplifying assumptions. For example, both biotite and muscovite occur at Coweeta, and both weather. However, given that they are present in subequal abundance and that muscovite typically weathers much more slowly than biotite, Velbel (1985a) assigned all K to biotite, effectively ascribing all K released from both micas to biotite. While this results in a slight over-estimate of the biotite weathering rate (by a proportion that depends on the relative abundances and relative weathering rates of the two micas), simplifications like this are often required in order to solve small systems of mass-balance equations (e.g., Bowser and Jones, 2002; Bricker et al., 2003). This specific approach anticipates informally the “fictive phase” approach formalized by Bowser and Jones (2002), Bricker et al. (2003), as already discussed above.

Another means to reduce the number of unknowns in watershed mass balance calculations is to “couple” primary and secondary phases as has been done for biotite and vermiculite in several previous studies (Cleaves et al., 1970; Velbel, 1985a; Taylor and Velbel, 1991) outlined above. Coupling refers here to the clay formation rate being calculated from its stoichiometric relationship with the weathering rate of a primary mineral. In the biotite-vermiculite coupling scenario, for each mole of biotite weathered, one mole of vermiculite would have to form (and hence the weathering rate of biotite would equal the formation rate of vermiculite). Other coupled reactant–product relationships may

also be invoked. For example, plagioclase and kaolinite (or gibbsite) are widely assumed to be stoichiometrically coupled, assuming conservation of Al. However, Velbel (1983) showed that secondary kaolinite forms from plagioclase by a dissolution-precipitation reaction in which all elements including Al are dissolved from plagioclase etch pits and reprecipitated elsewhere. In this case, kaolinite formation is by precipitation and is demonstrably not stoichiometrically coupled to plagioclase dissolution (Velbel, 1983, 1985a). The assumption of stoichiometric coupling between specific reactants and products is widely invoked, but not always justifiably.

A further disadvantage to the assumption of stoichiometric coupling is that the results of the mass balance will not accurately represent the decomposition of the secondary mineral and formation of a tertiary (or quaternary) phase. For example, in W2 at Coweeta secondary vermiculite may in reality continue weathering to tertiary kaolinite, and secondary or tertiary kaolinite may ultimately weather to tertiary or quaternary gibbsite. By uncoupling all primary and secondary phases, Price et al. (2005a) were able to calculate the weathering rates of vermiculite, kaolinite, and gibbsite, and demonstrated that all are currently forming in the regolith at Coweeta. Furthermore, Price et al. (2005a) found that the vermiculite formation rate is lower than the biotite destruction rate, indicating that some vermiculite is being further weathered to kaolinite, and/or gibbsite, and solutes.

3.3.2. Increasing the number of equations

Simplifying assumptions as discussed in the preceding section are one approach to addressing situations in which the number of unknowns to be solved for exceeds the number of mass-balance equations available. Another approach is to increase the number of mass-balance equations (construct and constrain mass-balance equations for more elements). However, increasing the number of equations may require consideration of additional minerals, simultaneously adding new unknowns. A requirement of mass-balance calculations is that for each solute measured in the stream waters, every phase involved in weathering (as determined through microscopy and other conventional mineralogical methods) that contains that element must also be included in the mass-balance. For example, Velbel (1985a) included Si in mass balances for Coweeta watersheds. However, the addi-

tional mass-balance equation for Si required consideration of kaolinite formation, which in turn required consideration of Al mass balance and therefore gibbsite. In this instance, the additional equations gained by including Si and Al mass balances require introduction of additional unknowns (i.e., the formation or destruction rates of kaolinite and gibbsite).

Consideration of some minor elements can add mass-balance equations and help overcome the problem of the number of unknowns exceeding the number of equations in watershed mass-balance. Price et al. (2005a) included mass-balance equations for the REE, La, Nd and Dy in their watershed mass-balance calculations of Coweeta watersheds. REE were selected based on their relatively high abundance (above background) in a preliminary scan of Coweeta stream waters. The relatively high concentrations of REE reflect the rapid weathering of metamict allanite at, or immediately below, the weathering front (Price et al., 2005b). The REE are well-suited for watershed mass balance studies because they are hosted by often rapidly weathering minerals such as metamict allanite (Price et al., 2005b) and garnet (Velbel, 1985; Price et al., 2005a), and because they are relatively mobile during weathering (e.g., Nesbitt, 1979; Cramer and Nesbitt, 1983; Banfield and Eggleton, 1989; Braun et al., 1990, 1993, 1998 and references therein; Marker and De Oliveira, 1990; Braun and Pagel, 1994; van der Weijden and van der Weijden, 1995; Koppi et al., 1996; Nesbitt and Markovics, 1997; Patino et al., 2003), with only small quantities being taken up by vermiculite at Coweeta. By having the additional equations, Price et al. (2005a) were able to

decouple biotite and vermiculite, retain the biomass term, and calculate the genesis rates of vermiculite, kaolinite and gibbsite. An example of their 8×8 coefficient matrix for Coweeta W2 is shown in Fig. 5. The differences in stoichiometric coefficients for the same minerals between Fig. 5 and Figs. 3 and 4 reflect additional EMPA data generated by Price et al. (2005a,b). The solution to the 8×8 matrix expression of Price et al. (2005a) (Fig. 5) is provided in Table 5. The trace elements chosen to expand a mass-balance matrix are largely site-specific. Strontium and Ba may also be possibilities depending on site mineralogy.

Bowser and Jones (2002) use a 10×10 matrix, because they have enough elements for which solute-mass-balance equations can be written. Where a natural system contains more phases (requiring more unknowns to be solved for), Bowser and Jones (2002) invoke several novel, systematic ways of reducing the number of unknowns to equal the number of mass-balance equations, thereby arriving at a mathematically unique solution for any given set of phases and their compositions. Where the compositions of one or more phases are difficult to constrain directly from mineralogical information, Bowser and Jones (2002) approach allows mass transfer coefficients to be calculated for a range of likely compositions of the “hard-to-constrain” phases.

The mass transfer coefficients so determined can be used to distinguish geologically permissible ranges of less-well-constrained phase compositions from geologically unreasonable compositional ranges. This is one way in which Bowser and Jones (2002) approach can be used to quantitatively state

	All	Plag	Garn	Biot	Verm	Kaol	Gibb	Biom		
Si	3.16	2.72	3.00	2.75	2.75	2.00	0.00	0.00	$\begin{bmatrix} \alpha_{All} \\ \alpha_{Plag} \\ \alpha_{Garn} \\ \alpha_{Biot} \\ \alpha_{Verm} \\ \alpha_{Kaol} \\ \alpha_{Gibb} \\ \alpha_{Biom} \end{bmatrix} = \begin{bmatrix} 1277 \\ 0 \\ 94.2 \\ 45.4 \\ 359 \\ 74.2 \\ 0.005 \\ 0.03 \end{bmatrix}$	
Al	2.22	1.28	2.00	1.57	1.81	2.00	1.00	0.00		
Mg	0.06	0.00	0.36	1.42	1.54	0.00	0.00	0.056		
Ca	1.58	0.28	0.41	0.001	0.026	0.00	0.00	0.144		
Na	0.16	0.72	0.00	0.041	0.032	0.00	0.00	0.008		
K	0.00	0.00	0.00	0.88	0.48	0.00	0.00	0.150		
Dy	0.000731	0.000000	0.0000565	0.0000	0.0000734	0.0000	0.0000	0.0000		
La	0.00533	0.000000	0.000000	0.0000	0.000506	0.0000	0.0000	0.0000		

Fig. 5. Example of an 8×8 coefficient matrix for Coweeta W2. Note inclusion of REE (Dy and La) and decoupling of all primary and secondary phases. Units of the stream flux (far right column vector) are $\text{mol ha}^{-1} \text{a}^{-1}$. All = allanite, Plag = plagioclase, Garn = almandine garnet, Biot = biotite, Verm = vermiculite, Kaol = kaolinite, Gibb = gibbsite, and Biom = biomass. After Price et al. (2005a).

Table 5
Comparison of mineral weathering rates calculated for Coweeta W2 with allanite and without allanite included in the mass balance

Mineral	Weathering Rates (mol ha ⁻¹ a ⁻¹)		
	Price et al. (2005a)	Taylor and Velbel (1991)	Percent difference (%)
Allanite	30	–	
Plagioclase	485	567	–14
Garnet	40	240	–83
Biotite	433	432	~0
Vermiculite	–308	–	
Kaolinite	–304	–	
Gibbsite	–288	–	
Biomass	–1060	–1232	–14

hypothetical ensembles of reactions in a manner that permits several kinds of tests of the hypotheses. Some tests of hypothesized ensembles of reactions can be derived directly from the calculations themselves. The most reasonable mass balances must be sought among those for which the resulting mass transfer coefficients satisfy elementary geological principles. For example, combinations of phases and phase compositions that yield mass transfer coefficients indicating that primary minerals form during weathering are physically unreasonable (as discussed by Bowser and Jones, 2002, p. 602). This simple test can be used to eliminate some hypothetical reaction ensembles. However, even after such elimination of some hypothetical reaction ensembles, multiple hypotheses may still remain (in other words, multiple alternative hypotheses may all give satisfactory results even after invoking this criterion to eliminate some others).

Other tests of hypothesized ensembles of reactions can involve seeking information from outside the calculations themselves. One such test would be to examine the mineral suites in the study area for the presence and composition of the hard-to-constrain phases. Finding that the actual phase composition of hard-to-constrain phases falls outside the “permissible” range of compositions that yield physically reasonable mass transfer coefficients (as in Bowser and Jones, 2002) would disprove that specific ensemble of hypothesized reactions, even if all the resulting mass transfer coefficients were geologically reasonable by the “no-formation-of-primary-minerals” criterion of the previous paragraph. In this manner, Bowser and Jones’ (2002) approach creates hitherto nonexistent opportunities to test reaction hypotheses and introduces to the mass balance literature new ways of eliminating

some hypothesized reaction ensembles from the broader range of otherwise (mathematically) acceptable results, thereby helping identify better (more geologically/mineralogically/geochemically reasonable) reaction ensembles from among all that might previously have been regarded as acceptable.

Bowser and Jones (2002) approach involves new ways of making the number of unknowns equal to the number of mass balance equations (n). They mention several other hypothesis-testing approaches besides the ones they develop. Among the alternatives they mention as having been beyond the scope of their paper, they mention (p. 597) the possibility of solving an $n - 1 \times n - 1$ matrix, to “use the resulting equations to calculate the value of solute concentration left out by using a smaller dimension matrix, and to compare the calculated and observed values” of the n th solute. The smaller the residual between the calculated and observed values of the n th solute species, the more completely the $n - 1 \times n - 1$ matrix describes the system of reactions. This manner of testing a hypothesized ensemble of reactions fits in the category of tests that can be implemented from the solute data and mass-balance alone. If several different $n - 1 \times n - 1$ matrices embodying several different hypothetical suites of mineral reactions (i.o.w., multiple working hypotheses) are used to calculate “predicted” abundances of the n th solute, the matrix producing the smaller residual might be favored. Furthermore, once formulated in this manner, geological and/or mineralogical data from outside the solute dataset might be sought. If evidence is found that does not refute the “least-residual” hypothesis, that hypothesis has survived a critical test, and must be accorded the status of a still-valid hypothetical explanation for the behavior of the system.

Bowser and Jones (2002) significantly advance the usefulness of solute-mass-balance approaches to the study of silicate weathering in natural systems. They develop a large-matrix spreadsheet method, and a systematic approach to dealing with systems in which the number of unknowns (phases for which mass transfer coefficients are being determined) exceeds the number of mass balance equations available. Their approach augments the literature on solute-mass-balance in several important ways: (1) It facilitates a “sensitivity analysis” approach to mass balance. In this approach, less-well-constrained mineralogical parameters are allowed to vary. This approach defines limits to ranges of input parameters, within which geologi-

cally/geochemically reasonable solutions to the mass balance equations result. (2) It advocates an uncommon but appropriately strong emphasis on the influence of secondary mineral compositions as important factors in arriving at geochemically reasonable mathematical solutions to mass-balance equations. (3) It permits study of the “comparative anatomy” of multiple watersheds and systems through a uniform methodological approach. (4) It applies widely available computational tools (spreadsheets) in support of the above 3 points. [Bowser and Jones \(2002\)](#) approach and conclusions are a valuable extension of the current state-of-the-art in mass-balance studies, permitting new approaches to hypothesis-testing that have not been easily invoked or widely applied previously. [Bowser and Jones \(2002\)](#) should stimulate a new cycle of mineralogically improved mass-balance studies. The approach of [Bowser and Jones \(2002\)](#) adds important and useful new dimensions to studies of mineral weathering rates in watersheds everywhere.

3.4. Calcium problem

[Bowser and Jones \(1993\)](#) introduced the term “calcium problem” to refer to the observation that solute analyses of many streams draining small watersheds underlain by crystalline silicate bedrock often contain Ca/Na ratios higher than can be predicted by congruent dissolution of plagioclase feldspar. In many granitic catchments, Ca/Na ratios in effluent solutions are significantly higher than the Ca/Na ratios of the plagioclase feldspars in the parent rocks ([Mast et al., 1990](#); [Velbel, 1992](#); [Stauffer and Wittchen, 1991](#); [Turk and Spahr, 1991](#); [Clow et al., 1997](#)). Uncertainty regarding the mineral source(s) of Ca is not a trivial concern. Calcium is normally the dominant base cation in the soil exchange complex, often to such an extent that it is the only base cation incorporated into many soil acidification models (e.g., [Reuss and Johnson, 1986](#)). Consequently, losses of Ca from, and replenishment rates of Ca to, the soil, are major factors in the susceptibility of landscapes and surface waters to acidification by acid deposition ([Lee and Schnoor, 1988](#); [Stauffer and Wittchen, 1991](#)). Therefore, Ca sources must be correctly identified for predictive modeling of surface-water responses to acidification ([Drever and Hurcomb, 1986](#); [Stauffer and Wittchen, 1991](#); [Turk and Spahr, 1991](#); [Clow et al., 1997](#)). The Ca problem has become an essential part of weathering studies ([Drever, 1997](#)).

In silicate-dominated natural hydrologic systems, plagioclase dissolution is commonly the most important weathering reaction ([Bowser and Jones, 1993, 2002](#); [Drever, 1997](#), [Jacobson et al., 2003](#)). Many previous studies of granitic or gneissic catchments suggest either non-stoichiometric dissolution of plagioclase feldspar, or dissolution of calcite, to explain excess Ca exports. [Clayton \(1986, 1988\)](#) concluded that preferential weathering of the calcic cores of zoned plagioclase in the Idaho batholith produced dissolved Ca/Na ratios significantly higher than the Ca/Na ratios of the parent feldspars. Other than differential weathering of zoned plagioclases ([Clayton, 1986, 1988](#)) or exsolution lamellae of different composition (“apparent incongruency” of [Gardner, 1983](#); [Inskip et al., 1991](#)), there is no compelling evidence for extensive non-stoichiometric leaching of naturally weathered feldspars ([Mast et al., 1990](#); [Velbel, 1993b](#); [Blum, 1994](#); [Blum and Stillings, 1995](#)). Zoned plagioclase is abundant and widespread in granitic batholiths ([Hyndman, 1972, p. 137](#); [Deer et al., 1963](#)), so that preferential weathering of calcic cores might occur in granitic landscapes. However, plagioclase in metamorphic rocks is compositionally homogenous (unzoned) ([Deer et al., 1963](#)), so high Ca/Na ratios in surface waters from schist and gneiss landscapes cannot be explained in this way.

[Aubert et al. \(2001, 2002\)](#) utilized Sr and Nd isotopic data, in combination with REE data, of springwaters from the Strengbach catchment in the Vosges Mountains of France, and determined that the springwater chemistry reflected a 15% contribution from apatite weathering. Similarly, from Sr isotope and Ca data of stream water draining a watershed located at Hubbard Brook Experimental Forest located in New Hampshire, USA, [Blum et al. \(2002\)](#) estimated that approximately 35% of the Ca was derived from the weathering of apatite.

Accessory calcite dissolution during weathering of silicate rocks may also contribute significant quantities of Ca to stream waters (e.g., [Velbel, 1992](#)), but is primarily a concern for recently glaciated or tectonically active landscapes ([Blum et al., 1998](#); [White et al., 1999](#)). [Blum et al. \(1998\)](#) found that trace amounts (~1%) of calcite found within granitoid rocks control stream water chemistry of glaciated northern Pakistan. Disseminated calcite in exfoliated granitoid rocks of recently glaciated (<10 Ka), high-elevation watersheds located in the western USA, contributes between 31 and 85 mole% Ca in discharge fluxes ([White et al., 1999](#)). [White](#)

et al. (1999) also found that watersheds located in geomorphically older landscapes (>200 Ka) such as Georgia, USA and Rio Icacos, Puerto Rico, did not exhibit Ca excesses beyond that explained by plagioclase feldspar weathering. Experimental studies of plagioclase and mica weathering have also concluded that in silicate-weathering environments the dissolution of disseminated calcite is limited by mechanical processes such as glaciation and tectonism that result in exposure of unweathered calcite to weathering solutions (Taylor et al., 2000a,b). Recently, Oliva et al. (2004) studied the high-elevation Estibère watershed in the French Pyrenees. They found that the trace calcic minerals apatite, epidote, prehnite and bytownite which represent ~1% of the total rock by volume are responsible for more than 80% of the Ca export from the watershed. The remaining Ca loss was attributed to oligoclase weathering. Oliva et al. (2004) noted allanite, hornblende and actinolite being present in the watershed bedrock, but did not invoke their weathering to be significant in the Ca budget.

At Coweeta dissolution of metamict allanite is an important source of Ca to stream waters (Price et al., 2005a,b). Despite constituting on average <1% of the Coweeta bedrock by volume, allanite contains a minimum of 25% of the bedrock Ca (Price et al., 2005b). To demonstrate the importance of highly weatherable accessory Ca-bearing phases in watershed mass-balance calculations, the results of Taylor and Velbel's (1991) mineral weathering rates are compared with that of Price et al. (2005a) for Coweeta W2 (Table 5). The large differences in garnet weathering rates reflects that, in the calculations of Taylor and Velbel (1991), a relatively high garnet weathering rate, and concomitantly relatively high plagioclase weathering, were necessary to account for all of the Ca in the stream waters. With allanite included in the calculations, a significantly lower (–83%; Table 5) and more geochemically reasonable garnet weathering rate is achieved. These results illustrate that mineral reactivity may be much more important in contributing solutes to weathering solutions than the total amount of mineral present (Bricker et al., 2003).

4. Discussion

Although watershed geochemical mass-balance methods are regarded as the most reliable means for making quantitative determinations of elemental transfers at the Earth's surface environment (Clay-

ton, 1979; Bricker et al., 2003), and perhaps the most accurate means of defining weathering reactions in natural systems (Bricker et al., 2003), there is a body of literature that criticizes these techniques. The challenge of studying natural systems in which mass-balance calculations may involve more unknowns than equations is discussed at length above. Other challenges and proposed solutions are briefly summarized in this section.

4.1. Use of assumed rather than actual mineral stoichiometries

Mass-balance studies may use idealized (“text-book”) mineral stoichiometries rather than mineral chemistries specific to individual study areas, a practice widely recognized as non-ideal (e.g., Finley and Drever, 1997; Bowser and Jones, 2002; Bricker et al., 2003) but nevertheless common. The use of specific mineral compositions provides a closer approximation to real geochemical behavior (Bowser and Jones, 2002; Bricker et al., 2003). Mineral formulae are readily determined from elemental oxide analyses determined by electron microprobe phase analyses (EMPA). If trace elemental concentrations are sufficiently high, then even their concentrations may be determined by EMPA. Price et al. (2005a,b) used laser ablation inductively-coupled plasma-mass spectrometry (LA-ICP-MS) to determine the concentrations of REE in the minerals involved in weathering at Coweeta. The only exceptions were kaolinite and gibbsite; however, these phases do not host REE (Burt, 1989) and have little compositional variability (Nesbitt, 1979; Duddy, 1980; Braun et al., 1993; Finley and Drever, 1997). LA-ICP-MS and other analytical technology are becoming increasingly available, and researchers may consider its use when characterizing the chemistry of mineral weathering for use in watershed geochemical mass-balance studies.

4.2. Weathering products determined using thermodynamics

In some studies, the secondary minerals forming during weathering have been determined using thermodynamic arguments from activity–activity diagrams (Finley and Drever, 1997). Drever and Zobrist (1992) demonstrated that the interpretation of mineral–water interactions based solely on phase diagrams may lead to spurious results. Identification of secondary minerals involved in chemical

weathering by microscopic observations and XRD data are preferable to assuming the occurrence and/or composition of secondary minerals.

4.3. Exclusion of a biomass term

As reviewed above, excluding a biomass term is only valid if the biomass is in steady state during the period of sampling. However, in forested watersheds the biomass is rarely in a steady state (Velbel, 1995; Drever, 1997). As discussed and demonstrated above, Taylor and Velbel (1991) determined that exclusion of a biological term from Coweeta watershed mass balance calculations can result in underestimation of mineral weathering rates by up to a factor of almost 4 (Table 4). In the Coweeta example, this factor of 4 weathering rate underestimation was for biotite, and reflects the biological influence on K biogeochemistry. Plagioclase feldspar weathering is much less influenced by biomass because its dissolution rate is determined largely by the Na flux, which is only minimally influenced by biological processes (Figs. 4 and 5; Taylor and Velbel, 1991; Velbel, 1993a).

When addressing the role of biomass in calculations of mineral weathering rates using watershed mass-balance methods, the depth in the regolith at which a mineral weathers may be as important as whether or not the mineral contains plant nutrients. A mineral that is rapidly destroyed at the weathering front of a thick regolith (e.g., several meters) will not survive into the rhizosphere and be influenced by biological processes. Under such circumstances the stream water chemistry will simply reflect the inorganic weathering of such a phase (Bricker et al., 2003). At Coweeta, metamict allanite dissolves rapidly at, or slightly below, the weathering front of an approximately 6 m thick saprolite (Price et al., 2005b). Biotite is also weathering to vermiculite at or near the weathering front, and thus the vermiculite is able to take up REE released by the allanite (Fig. 5). Since the vermiculite persists into the solum at Coweeta, the biomass may potentially consume REE. This discussion underscores the importance of mineralogical and chemical characterization of a watershed's regolith prior to determining the influence of biomass on stream water chemistry. Hypothetically, if all of the primary minerals weathering in a watershed were determined to be dissolving below the rhizosphere, then exclusion of a biomass term in a mass-balance study may be acceptable. Another possibility is that only certain

minerals survive into the rhizosphere. In that case, the biomass stoichiometry may be reduced to include only those plant nutrients contained in the surviving minerals.

4.4. Future directions in watershed mass-balance calculations

One major area deserving additional attention is quantification of uncertainty in solute budgets and on the calculated weathering rates. All measurements of precipitation and streamflow have some measurement error, as do chemical measurements and resultant fluxes. The consequent uncertainty for calculated mineral weathering rates could be an important factor in comparisons between different watersheds (e.g., for establishing whether the calculated values are significantly different), as well as for comparing different solutions for any given system (see Section 3.3.2). With the increasing abundance of geochemical data, it might in many cases be possible to construct systems of equations in which the number of mass balance equations exceeds the number of unknowns. Statistical approaches could help rigorously determine the best (out of all possible) fits in such systems.

Most published papers that retrieve weathering rates of individual minerals from the overall input–output behavior of watershed systems by approaches like those described in this paper use long-term average fluxes representing periods of record of years or in some instances several decades. A very few have solved systems of equations to calculate weathering rates for shorter periods of time (e.g., water years, seasons, hydrologic events). Simple mathematical approaches for long-term averages (Velbel, 1986; Taylor and Velbel, 1991) do not transfer directly to shorter timescales. The assumption of steady-state behavior of the system that is built into the most commonly used forms of the mass balance equations (Velbel, 1986; Taylor and Velbel, 1991) is relatively easy to justify over long periods of record, but as shorter time-scales are modeled, transient and non-steady-state behaviors become important. In such instances, the proper approach requires more than merely modeling, for example, successive water years using the same system of equations with different annual fluxes; even if each water year is treated as steady-state, the transition from one water year to the next involves a mathematically important discontinuity between the two steady states. However, even

though the mathematics become more complicated, the potential reward of such an approach is great. Being able to calculate weathering rates for seasons of biomass growth with those for dormant seasons, for example, might be one way to shed useful insight into the role of macrobiota on silicate weathering rates, a topic of considerable current interest among researchers working on the role of weathering in the global geochemical C cycle (e.g., Berner et al., 1983; Berner, 1995; Berner and Kothavala, 2001; Berner and Berner, 2003).

Although sufficient databases (i.e., minimum 7-a record of hydrologic, and stream and precipitation chemistry data; Likens and Bormann, 1995) exist for major elements at many sites, comparable data for REE and other applicable trace elements are needed. Again, with the advent of the ICP-MS, chemical analyses for trace elements in both solid and aqueous phases are becoming increasingly routine. At Coweeta, REE were utilized in order to permit establishment of the additional equations to solve for all of the unknowns. Furthermore, if it is determined that REE-bearing phases (either primary or secondary) persist into the rhizosphere, then REE stoichiometries should be included in biomass terms as well. Although poorly understood, vegetation is known to take up REE (e.g., Kabata-Pendias, 2001; Shan et al., 2005). Future studies, therefore, may include long-term precipitation and stream water sampling for trace elements. In addition, the combination of biomass trace element stoichiometric data with major element stoichiometric data should be investigated. More complete sampling and analysis of a larger suite of elements (both dissolved and in the solid phases) would be a promising line of future research.

Much remains to be done regarding the interactions of biological and geochemical processes in small watersheds. An applicable biomass term for use in watershed mass-balance calculations is dependent on site-specific characteristics. Because the assumption of biomass being in steady-state is rarely true, a better justification for exclusion of a biomass term is if none of the minerals involved in weathering survive into the rhizosphere. The biomass term should also include a stoichiometry for any element included in the stream flux data, and that is contained in minerals that experience biologically-mediated weathering in the rhizosphere. Solving for botanical fluxes as additional unknowns may allow watershed mass balances to provide addi-

tional insight into the ecological state of the watershed's ecosystem (e.g., Taylor and Velbel, 1991; Velbel, 1995). Application of a fictive-phase-like approach to biomass interactions with watershed solute cycling (e.g., Taylor and Velbel, 1991; Velbel, 1995) may allow improved incorporation of botanical nutrient-cycling effects into studies of mineral-weathering rates, an important area of uncertainty in current global geochemical C-cycle models (e.g., Berner and Kothavala, 2001; Berner and Berner, 2003).

Determination of the degree to which formation rates of specific secondary minerals are stoichiometrically coupled to the weathering rates of specific reactant minerals is another potentially fruitful avenue for future research. Further research in any individual watershed may reveal that some reactant-product pairs are stoichiometrically coupled through structural (e.g., biotite-vermiculite) or thermodynamic (e.g., Al-conservation; feldspar-kaolinite) controls. If so, in those specific watersheds, the number of unknowns that need to be solved for can be reduced relative to the number of available mass-balance equations.

5. Summary and conclusions

Solute-based watershed geochemical mass-balance methods are a powerful and accurate technique for quantifying mineral weathering rates in the field. However, to provide the closest possible approximation to real geochemical behavior of complex natural systems, the following data are needed.

- (1) A watershed of known area developed on crystalline bedrock with no evidence of water loss to ground water;
- (2) Identification through microscopy and XRD of the minerals involved in weathering;
- (3) Determination of the stoichiometric formulae by EMPA (and possibly LA-ICP-MS) of all minerals determined to be involved in weathering;
- (4) Measurement of stream discharge and weekly stream solute chemistry for a period of record sufficient to justify selection of a representative long-term average value (if a single long-term average value satisfies the study design; Likens and Bormann, 1995, suggest a minimum 7-a period, but shorter periods of record still allow annual, seasonal and/or event-based mass balance), with analyses of enough solutes to

- permit the number of equations to equal the number of unknowns (i.e., mineral weathering rates and rate of nutrient uptake by biomass);
- (5) Measurement of the amount and chemical composition of bulk precipitation (also weekly and for a minimum 7-a period; Likens and Bormann, 1995) for each solute quantified in the stream water in order to permit subtraction of precipitation input fluxes from stream output fluxes;
 - (6) Quantification of a biomass elemental uptake stoichiometry appropriate for the watershed being studied.

For an ideal watershed mass-balance study, data in all six of these categories would be available. However, this is rarely the case, even at a well studied site such as the Coweeta Hydrologic Laboratory. Numerous research teams have used watershed solute mass-balance to gain insight into weathering rates of minerals in nature, with considerable success to date despite the complexity of the natural systems and the limitations of the mass-balance approach. Numerous improvements to the approach are possible, thanks to developments in analytical and computational capabilities. It can be reasonably expected that some of these improvements will expand the range of natural phenomena that can be fruitfully studied using watershed solute mass-balance, thereby providing still more scientific insight into a broad range of biogeochemical problems in the future.

Acknowledgements

We express our thanks to Dr. Jennifer Knoepp, Research Soil Scientist at Coweeta, for her assistance and cooperation in the field in the most recent cycles of work at Coweeta. M. Velbel thanks all his former students and collaborators who joined in studying weathering at Coweeta over the past two decades. Thanks also to Lina Patino, David Szymanski and Meredith Lindeman for their help with stream water sampling and analyses for the REE. Funding for projects associated with this manuscript have been partially provided by NSF Grants EAR 80-07815 (to R.A. Berner) and BSR 85-14328 (to D.A. Crossley, Jr.), a Grant-in-Aid of Research, from Sigma Xi, The Scientific Research Society; a Michigan Space Grant Consortium Graduate Fellowship; and a Clay Minerals Society Student Grant. We also express our thanks to

Candace Martin, Lee Ann Munk and A. Joshua West, for their constructive reviews of the manuscript.

References

- Affi, A.A., Bricker, O.P., 1983. Weathering reactions, water chemistry and denudation rates in drainage basins of different bedrock types: I – sandstone and shale. *Proceedings of Hamburg Symposium on Dissolved Loads of Rivers and Surface Water Quantity/Quality Relationships*. IAHS Publication #141, pp. 193–203.
- April, R.R., Newton, R., Coles, L.T., 1986. Chemical weathering in two Adirondack watersheds: past and present-day rates. *Geol. Soc. Am. Bull.* 97, 1232–1238.
- Aubert, D., Stille, P., Probst, A., 2001. REE fractionation during granite weathering and removal by waters and suspended loads: Sr and Nd isotopic evidence. *Geochim. Cosmochim. Acta* 65, 387–406.
- Aubert, D., Stille, P., Probst, A., Gauthier-Lafaye, F., Pourcelot, L., Del nero, M., 2002. Characterization and migration of atmospheric REE in soils and surface waters. *Geochim. Cosmochim. Acta* 66, 3339–3350.
- Banfield, J.F., Eggleton, R.A., 1988. Transmission electron microscopy of biotite weathering. *Clays Clay Miner.* 36, 47–60.
- Banfield, J.F., Eggleton, R.A., 1989. Apatite replacement and rare earth mobilization, fractionation, and fixation during weathering. *Clays Clay Miner.* 37, 113–127.
- Becker, G.F., 1895. Reconnaissance of the gold fields of the southern Appalachians. In: US Geological Survey 16th Annual Report, 1894-1895, Part 3, US Government Printing Office, Washington, DC, pp. 251–331.
- Berner, R.A., 1995. Chemical weathering and its effect on atmospheric CO₂ and climate. In: White, A.F., Brantley, S.B. (Eds.), *Chemical Weathering Rates of Silicate Minerals*, vol. 31. Mineralogical Society of America, Washington, DC, pp. 565–583 (Chapter 13).
- Berner, E.K., Berner, R.A., 2003. Plants and mineral weathering: Past and present. In: Holland, H.D., Turekian, K.K. (Ex. Eds.), Drever, J.I. (Ed.), *Treatise on Geochemistry*, vol. 5, Surface and Ground Water, Weathering, and Soils, Elsevier, New York, pp. 169–188.
- Berner, R.A., Kothavala, Z., 2001. GEOCARB III: a revised model of atmospheric CO₂ over Phanerozoic time. *Am. J. Sci.* 301, 182–204.
- Berner, R.A., Lasaga, A.C., Garrels, R.M., 1983. The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. *Am. J. Sci.* 284, 641–683.
- Berry, J.L., 1976. Study of chemical weathering in Coweeta Hydrologic Laboratory, Macon County, North Carolina. Unpublished report on file at the Coweeta Hydrologic Laboratory.
- Blum, A.E., 1994. Feldspars in weathering. In: Parsons, I. (Ed.), *Feldspars and their reactions*. NATO Advanced Study Institute. Kluwer Academic Publishers., The Netherlands, pp. 595–629.
- Blum, A.E., Stillings, L.L., 1995. Feldspar dissolution kinetics. In: White, A.F., Brantley, S.L. (Eds.), *Chemical weathering rates of silicate minerals*, *Reviews in Mineralogy*, vol. 31. Mineralogical Society of America, Washington, DC, pp. 291–351 (Chapter 7).

- Blum, J.D., Gazis, C.A., Jacobson, A.D., Chamberlain, C.P., 1998. Carbonate versus silicate weathering in the Raikhot watershed within the High Himalayan Crystalline Series. *Geology* 26, 411–414.
- Blum, J.D., Klaue, A., Nezat, C.A., Driscoll, C.T., Johnson, C.E., Siccama, T.G., Eager, C., Fahey, T., Likens, G.E., 2002. Mycorrhizal weathering of apatite as an important calcium source in base-poor forest ecosystems. *Nature* 417, 729–731.
- Boring, L.R., Monk, C.D., Swank, W.T., 1981. Early regeneration of a clear-cut southern Appalachian forest. *Ecology* 62, 1244–1253.
- Bowser, C.J., Jones, B.F., 1993. Mass balances of natural water: silicate dissolution, clays, and the calcium problem. In: *Biogeochem. Symp. Ecosystem Behavior: Evaluation of Integrated Monitoring in Small Catchments*, Prague, Czech Republic, pp. 30–31.
- Bowser, C.J., Jones, B.F., 2002. Mineralogic controls on the composition of natural waters dominated by silicate hydrolysis. *Am. J. Sci.* 32, 582–662.
- Brantley, S.L., 2003. Reaction kinetics of primary rock-forming minerals under ambient conditions. In: Holland, H.D., Turekian, K.K. (Ex. Eds.), Drever, J.I. (Ed.), *Treatise on Geochemistry*, vol. 5, Surface and Ground Water, Weathering, and Soils, Elsevier, New York, pp. 73–117.
- Braun, J.-J., Pagel, M., 1994. Geochemical and mineralogical behavior of REE, Th, and U in the Akongo lateritic profile (SW Cameroon). *Catena* 21, 173–177.
- Braun, J.-J., Pagel, M., Muller, J.P., Bilong, P., Michard, A., Guillet, B., 1990. Cerium anomalies in lateritic profiles. *Geochim. Cosmochim. Acta* 51, 597–605.
- Braun, J.-J., Pagel, M., Herbillon, A., Rosin, C., 1993. Mobilization and redistribution of REE and thorium in a syenitic lateritic profile: a mass balance study. *Geochim. Cosmochim. Acta* 57, 4419–4434.
- Braun, J.-J., Viers, J., Dupré, B., Ndam, J., Muller, J.-P., 1998. Solid/liquid REE fractionation in the lateritic system of Goyoum, East Cameroon: the implications for the present dynamics of the soil covers of the humid tropical regions. *Geochim. Cosmochim. Acta* 62, 273–299.
- Bricker, O.P., 1986. Geochemical investigations of selected Eastern United States watersheds affected by acid deposition. *J. Geol. Soc., London* 143, 621–626.
- Bricker, O.P., Rice, K.C., 1989. Acidic deposition to streams. *Environ. Sci. Technol.* 23, 379–385.
- Bricker, O., Katz, B., Afifi, A., Puckett, L., Olson, C., Kennedy, M., 1983. Geochemistry of small Appalachian watersheds developed on silicate bedrock. *Sci. Géol. Mém.* 73, 41–52.
- Bricker, O.P., Jones, B.F., Bowser, C.J., 2003. Mass-balance approach to interpreting weathering reactions in watershed systems. In: Holland, H.D., Turekian, K.K. (Ex. Eds.), Drever, J.I. (Ed.), *Treatise on Geochemistry*, vol. 5, Surface and Ground Water, Weathering, and Soils, Elsevier, New York, pp. 119–132 (Chapter 4).
- Brimhall, G.H., Dietrich, W.E., 1987. Constituent mass balance relations between chemical composition, volume, density, porosity, and strain in metasomatic hydrochemical systems: results on weathering and pedogenesis. *Geochim. Cosmochim. Acta* 51, 567–587.
- Burt, D.M., 1989. Compositional and phase relations among rare earth element minerals. In: Lipin, B.R., McKay, G.A. (Eds.), *Geochemistry and mineralogy of rare earth elements*, Reviews in Mineralogy, vol. 21. Mineralogical Society of America, Washington, DC, pp. 259–308.
- Ciampone, M.A., 1995. Non-systematic weathering profile on metamorphic rock in the southern Blue Ridge Mountains, North Carolina: Petrography, bulk chemistry, and mineral chemistry of biotite. Unpublished M.S. thesis, University of Cincinnati.
- Clayton, J.L., 1979. Nutrient supply to soil by rock weathering. In: *Impact of Intensive Harvesting on Forest Nutrient Cycling*. State University of New York, College of Environmental Science and Forestry, Syracuse, pp. 75–96.
- Clayton, J.L., 1986. An estimate of plagioclase weathering rate in the Idaho batholith based upon geochemical transport rates. In: Colman, S.M., Dethier, D.P. (Eds.), *Rates of Chemical Weathering of Rocks and Minerals*. Academic Press, New York, pp. 453–467 (Chapter 19).
- Clayton, J.L., 1988. Some observations on the stoichiometry of feldspar hydrolysis in granitic soil. *J. Environ. Qual.* 17, 153–157.
- Cleaves, E.T., Godfrey, A.E., Bricker, O.P., 1970. Geochemical balance of a small watershed and its geomorphic implications. *Geol. Soc. Am. Bull.* 81, 3015–3032.
- Cleaves, E.T., Fisher, D.W., Bricker, O.P., 1974. Chemical weathering of serpentinite in the eastern Piedmont of Maryland. *Geol. Soc. Am. Bull.* 85, 437–444.
- Clow, D.W., Mast, M.A., Bullen, T.D., Turk, J.T., 1997. Strontium 87/strontium 86 as a tracer of mineral weathering reactions and calcium sources in an alpine/subalpine watershed, Loch Vale, Colorado. *Water Resour. Res.* 33, 1335–1351.
- Cramer, J.J., Nesbitt, H.W., 1983. Mass-balance relations and trace-element mobility during continental weathering of various igneous rocks. *Sci. Géol. Mém.* 73, 63–73.
- Creasey, J., Edwards, A.C., Reid, J.M., MacLoud, D.A., Cresser, M.S., 1986. The use of catchment studies for assessing chemical weathering rates in two contrasting upland areas in northeast Scotland. In: Colman, S.M., Dethier, D.P. (Eds.), *Rates of Chemical Weathering of Rocks and Minerals*. Academic Press, New York, pp. 467–502 (Chapter 20).
- Day, F.P., Monk, C.D., 1977. Seasonal nutrient dynamics in the vegetation on a southern Appalachian watershed. *Am. J. Bot.* 64, 1126–1139.
- Deer, W.A., Howie, R.A., Zussman, J., 1963. *Rock-Forming Minerals, Framework Silicates*, vol. 4. Longmans, London.
- Delvigne, J., 1998. *Atlas of Micromorphology of Mineral Alteration and Weathering*. Canadian Mineral. Special Publication, 3.
- Drever, J.I., 1997. Catchment mass balance. In: Saether, O.M., de Caritat, A.A. (Eds.), *Geochemical Processes, Weathering and Ground water Recharge in Catchments*. Balkema, Rotterdam, Netherlands, pp. 241–261 (Chapter 9).
- Drever, J.I., Hurcomb, D.R., 1986. Neutralization of atmospheric acidity by chemical weathering in an alpine drainage basin in the North Cascade Mountains. *Geology* 14, 221–224.
- Drever, J.I., Zobrist, J., 1992. Chemical weathering of silicate rocks as a function of elevation in the southern Swiss Alps. *Geochim. Cosmochim. Acta* 56, 3209–3216.
- Duddy, I.R., 1980. Redistribution and fractionation of rare earth and other elements in a weathering profile. *Chem. Geol.* 30, 363–381.
- Feth, J.H., Roberson, C.E., Polzer, W.L., 1964. Sources of mineral constituents in water from granitic rocks Sierra

- Nevada, California and Nevada. US Geological Survey Prof. Pap. 1535-I.
- Finley, J.B., Drever, J.I., 1997. Chemical mass balance and rates of mineral weathering in a high-elevation catchment, West Glacier Lake, Wyoming. *Hydrol. Proc.* 11, 745–764.
- Furman, T., Thompson, P., Hatchl, B., 1998. Primary mineral weathering in the central Appalachians: a mass balance approach. *Geochim. Cosmochim. Acta* 62, 2889–2904.
- Gardner, L.R., 1980. Mobilization of Al and Ti during rock weathering – isovolumetric geochemical evidence. *Chem. Geol.* 30, 151–165.
- Gardner, L.R., 1983. Mechanisms and kinetics of incongruent feldspar dissolution. *Geology* 11, 418–421.
- Gardner, L.R., Kheoruenromne, I., Chen, H.S., 1978. Isovolumetric geochemical investigation of a buried granite saprolite near Columbia, SC, USA. *Geochim. Cosmochim. Acta* 42, 417–424.
- Gardner, L.R., Kheoruenromne, I., Chen, H.S., 1981. Geochemistry and mineralogy of an unusual diabase saprolite near Columbia, South Carolina. *Clays Clay Miner.* 29, 184–190.
- Garrels, R.M., 1967. Genesis of some ground waters from igneous rocks. In: Abelson, P.H. (Ed.), *Researches in Geochemistry*, vol. 2. Wiley, New York, pp. 405–420.
- Garrels, R.M., Mackenzie, F.T., 1967. Origin of the chemical compositions of some springs and lakes. In: Stumm, W. (Ed.), *Equilibrium Concepts in Natural Water Systems*, *Advances in Chemistry Series*, 67. American Chemical Society, pp. 222–242 (Chapter 10).
- Grantham, J.H., Velbel, M.A., 1988. The influence of climate and topography on rock-fragment abundance in modern fluvial sands of the southern Blue Ridge Mountains, North Carolina. *J. Sed. Pet.* 58, 219–227.
- Hatcher, R.D., 1980. Geologic map of Coweeta Hydrologic Laboratory, Prentiss Quadrangle, North Carolina. State of North Carolina, Department of Natural Resources and Community Development, in Cooperation with the Tennessee Valley Authority. Scale 1:14,400.
- Hatcher, R.D., 1988. Bedrock geology and regional geologic setting of Coweeta Hydrologic Laboratory in the Eastern Blue Ridge. In: Swank, W.T., Crossley, D.A. (Eds.), *Forest Hydrology and Ecology at Coweeta*. Springer, NY, pp. 81–92 (Chapter 5).
- Helvey, J.D., Patric, J.H., 1988. Research on interception losses and soil moisture relationships. In: Swank, W.T., Crossley, D.A. (Eds.), *Forest Hydrology and Ecology at Coweeta*. Springer, New York, pp. 129–137 (Chapter 9).
- Hewlett, J.D., 1961. Soil moisture as a source of base flow from steep mountain watersheds. Southeastern Forest Experiment Station Paper No. 132. US Department of Agriculture-Forest Service, Asheville, North Carolina.
- Hewlett, J.D., Hibbert, A.R., 1963. Moisture and energy conditions within a sloping soil mass during drainage. *J. Geophys. Res.* 68, 1081–1087.
- Hyndman, D.W., 1972. *Petrology of Igneous and Metamorphic Rocks*. McGraw-Hill, New York.
- Inskeep, W.P., Nater, E.A., Bloom, P.R., Vandervoort, D.S., Erich, M.S., 1991. Characterization of laboratory weathered labradorite surfaces using X-ray photoelectron spectroscopy and transmission electron microscopy. *Geochim. Cosmochim. Acta* 55, 787–800.
- Jacobson, A.D., Blum, J.D., Chamberlain, C.P., Craw, D., Koons, P.O., 2003. Climatic and tectonic controls on chemical weathering in the New Zealand Southern Alps. *Geochim. Cosmochim. Acta* 67, 29–46.
- Kabata-Pendias, A., 2001. *Trace Elements in Soils and Plants*. CRC Press, New York.
- Katz, B.G., 1989. Influence of mineral weathering reactions on the chemical composition of soil water, springs, and ground water, Catoctin Mountains, Maryland. *Hydrol. Proc.* 3, 185–202.
- Katz, B.G., Bricker, O.P., Kennedy, M.M., 1985. Geochemical mass-balance relationships for selected ions in precipitation and stream water, Catoctin Mountains, Maryland. *Am. J. Sci.* 285, 931–962.
- Koppi, A.J., Edis, R., Field, D.J., Geering, H.R., Klessa, D.A., Cockayne, D.J.H., 1996. Rare earth element trends and cerium–uranium–manganese associations in weathered rock from Koongarra, Northern Territory, Australia. *Geochim. Cosmochim. Acta* 60, 1695–1707.
- Lee, S., Schnoor, J.L., 1988. Reactions that modify chemistry in lakes of the National Surface Water Survey. *Environ. Sci. Technol.* 22, 190–195.
- Likens, G.E., Bormann, F.B., 1995. *Biogeochemistry of a Forested Ecosystem*. Springer-Verlag, New York.
- Marker, A., De Oliveira, J.J., 1990. The formation of rare earth element scavenger minerals in the weathering products derived from alkaline rocks of SE-Bahia, Brazil. *Chem. Geol.* 84, 373–374.
- Marschner, H., 1995. *Mineral Nutrition in Higher Plants*. 2nd ed.. Academic Press, San Diego, CA.
- Mast, M.A., Drever, J.I., Baron, J., 1990. Chemical weathering in the Loch Vale watershed, Rocky Mountain National Park, Colorado. *Water Resour. Res.* 26, 2971–2978.
- Miller, C.F., Hatcher Jr., R.D., Ayers, J.C., Coath, C.D., Harrison, T.M., 2000. Age and zircon inheritance of eastern Blue Ridge plutons, southwestern North Carolina and northeastern Georgia, with implications for magma history and evolution of the southern Appalachian orogen. *Am. J. Sci.* 300, 142–172.
- Mills, H.H., Brackenridge, G.R., Jacobson, R.B., Newell, W.L., Pavich, M., Pomery, J.S., 1987. Appalachian mountains and plateaus. In: Graf, W.L. (Ed.), *Geomorphic Systems of North America*, Geological Society of America Centennial Special, Vol. 2. Geological Society of America, Boulder, CO, pp. 5–50.
- Moulton, K.L., West, J., Berner, R.A., 2000. Solute flux and mineral mass balance approaches to the quantification of plant effects on silicate weathering. *Am. J. Sci.* 300, 539–570.
- Nahon, D.B., 1991. *Introduction to the Petrology of Soils and Chemical Weathering*. Wiley, New York.
- Nesbitt, H.W., 1979. Mobility and fractionation of rare earth elements during weathering of granodiorite. *Nature* 279, 206–210.
- Nesbitt, H.W., Markovics, G., 1997. Weathering of granodiorite crust, long-term storage of elements in weathering profiles, and petrogenesis of siliclastic sediments. *Geochim. Cosmochim. Acta* 61, 1653–1670.
- Newman, A.C.D., 1987. *Chemistry of Clays and Clay Minerals*. Wiley, New York.
- Oliva, P., Dupré, B., Martin, F., Viers, J., 2004. The role of trace minerals in chemical weathering in a high-elevation granitic watershed (Estibère, France): chemical and mineralogical evidence. *Geochim. Cosmochim. Acta* 68, 2223–2244.

- Pačes, T., 1983. Rate constants of dissolution derived from the measurements of mass balance in hydrological catchments. *Geochim. Cosmochim. Acta* 47, 1855–1863.
- Pačes, T., 1986. Rates of weathering and erosion derived from mass balance in small drainage basins. In: Colman, S.M., Dethier, D.P. (Eds.), *Rates of Chemical Weathering of Rocks and Minerals*. Academic Press, New York, NY, pp. 531–550 (Chapter 22).
- Patino, L.C., Velbel, M.A., Price, J.R., Wade, J.A., 2003. Trace element mobility during spheroidal weathering of basalts and andesites in Hawaii and Guatemala. In: Anderson, S.P., Blum, A.E. (Eds.), *Controls on Chemical Weathering*. *Chem. Geol.* 202, pp. 343–364.
- Plummer, L.N., Back, W., 1980. The mass balance approach: application to interpreting the chemical evolution of hydrologic systems. *Am. J. Sci.* 280, 130–142.
- Price, J.R., Velbel, M.A., 2003. Chemical weathering indices applied to weathering profiles developed on heterogeneous felsic metamorphic parent rocks. In: Anderson, S.P., Blum, A.E. (Eds.), *Controls on Chemical Weathering*. *Chem. Geol.* 202, pp. 397–416.
- Price, J.R., Velbel, M.A., Patino, L.C., 2005a. Rates and timescales of clay-mineral formation by weathering in saprolitic regoliths of the southern Appalachians from geochemical mass balance. *Geol. Soc. Am. Bull.* 117, 783–794.
- Price, J.R., Velbel, M.A., Patino, L.C., 2005b. Allanite and epidote weathering at the Coweeta Hydrologic Laboratory, western North Carolina, USA. *Am. Mineral.* 90, 101–114.
- Reuss, J.O., Johnson, D.W., 1986. *Acid Deposition and the Acidification of Soils and Waters*, Ecological Studies, Series No. 59. Springer, New York.
- Riebe, C.S., Kirchner, J.W., Finkel, R.C., 2003. Long-term rates of chemical weathering and physical erosion from cosmogenic nuclides and geochemical mass balance. *Geochim. Cosmochim. Acta* 67, 4411–4427.
- Riebe, C.S., Kirchner, J.W., Finkel, R.C., 2004a. Sharp decrease in long-term chemical weathering rates along an altitudinal transect. *Earth Planet. Sci. Lett.* 218, 421–434.
- Riebe, C.S., Kirchner, J.W., Finkel, R.C., 2004b. Erosional and climatic effects on long-term chemical weathering rates in granitic landscapes spanning diverse climate regimes. *Earth Planet. Sci. Lett.* 224, 547–562.
- Shan, X.Q., Zhang, S., Wen, B., 2005. Fractionation and bioavailability of rare earth elements in soils. In: Shtangeeva, I. (Ed.), *Trace and Ultratrace Elements in Plants and Soils*. WIT Press, Cambridge, pp. 249–286 (Chapter 10).
- Stauffer, R.E., Wittchen, B.D., 1991. Effects of silicate weathering on water chemistry in forested, upland, felsic terrane of the USA. *Geochim. Cosmochim. Acta* 55, 3253–3271.
- Swank, W.T., Douglass, J.E., 1977. Nutrient budgets for undisturbed and manipulated hardwood forest ecosystems in the mountains of North Carolina. In: Correll, D.L. (Ed.), *Watershed Research in Eastern North America*. Smithsonian Institution, Washington, DC, pp. 343–364.
- Swank, W.T., Waide, J.B., 1988. Characterization of baseline precipitation and stream chemistry and nutrient budgets for control watersheds. In: Swank, W.T., Crossley, D.A. (Eds.), *Forest Hydrology and Ecology at Coweeta*. Springer, New York, pp. 57–79 (Chapter 4).
- Swift Jr., L.W., Cunningham, G.B., Douglass, J.E., 1988. Characterization of baseline precipitation and stream chemistry and nutrient budgets for control watersheds. In: Swank, W.T., Crossley, D.A. (Eds.), *Forest Hydrology and Ecology at Coweeta*. Springer, New York, pp. 35–56 (Chapter 3).
- Taylor, G., Eggleton, R.A., 2001. *Regolith Geology and Geomorphology*. Wiley, New York.
- Taylor, A.B., Velbel, M.A., 1991. Geochemical mass balances and weathering rates in forested watersheds of the southern Blue Ridge II. Effects of botanical uptake terms. *Geoderma* 51, 29–50.
- Taylor, A.S., Blum, J.D., Lasaga, A.C., 2000a. The dependence of labradorite dissolution and Sr isotope release rates on solution saturation state. *Geochim. Cosmochim. Acta* 64, 2389–2400.
- Taylor, A.S., Blum, J.D., Lasaga, A.C., MacInnis, I.N., 2000b. Kinetics of dissolution and Sr release during biotite and phlogopite weathering. *Geochim. Cosmochim. Acta* 64, 1191–1208.
- Turk, J.T., Spahr, N.E., 1991. Rocky Mountains. In: Charles, D.F. (Ed.), *Acidic Deposition and Aquatic Ecosystems – Regional Case Studies*. Springer, New York, pp. 471–501.
- van der Weijden, C.H., van der Weijden, R.D., 1995. Mobility of major, minor and some redox-sensitive trace elements and rare-earth elements during weathering of four granitoids in central Portugal. *Chem. Geol.* 125, 149–167.
- Velbel, M.A., 1983. A dissolution-reprecipitation mechanism for the pseudomorphous replacement of plagioclase feldspars by clay minerals during weathering. In: Nahon, D., Noack, Y. (Eds.), *Pétrologie des Altérations et des Sols*, vol. II. *Sciences Géologiques, Mémoires (Strasbourg)* 71, pp. 139–147.
- Velbel, M.A., 1984. Natural weathering mechanisms of almandine garnet. *Geology* 12, 631–634.
- Velbel, M.A., 1985a. Geochemical mass balances and weathering rates in forested watersheds of the southern Blue Ridge. *Am. J. Sci.* 285, 904–930.
- Velbel, M.A., 1985b. Hydrogeochemical constraints on mass balances in forested watersheds of the southern Appalachians. In: Drever, J.I. (Ed.), *The Chemistry of Weathering*. D. Reidel, Holland, pp. 231–247.
- Velbel, M.A., 1986. The mathematical basis for determining rates of geochemical and geomorphic processes in small forested watersheds by mass balance: examples and implications. In: Colman, S.M., Dethier, D.P. (Eds.), *Rates of Chemical Weathering of Rocks and Minerals*. Academic Press, New York, pp. 439–451 (Chapter 18).
- Velbel, M.A., 1988. Weathering and soil-forming processes. In: Swank, W.T., Crossley, D.A. (Eds.), *Forest Hydrology and Ecology at Coweeta*. Springer, New York, pp. 93–102 (Chapter 6).
- Velbel, M.A., 1990. Mechanisms of saprolitization, isovolumetric weathering, and pseudomorphous replacement during rock weathering – a review. *Chem. Geol.* 84, 17–18.
- Velbel, M.A., 1992. Geochemical mass balances and weathering rates in forested watersheds of the southern Blue Ridge III. Cations budgets and the weathering rate of amphibole. *Am. J. Sci.* 292, 58–78.
- Velbel, M.A., 1993a. Temperature dependence of silicate weathering in nature: How strong a negative feedback on long-term accumulation of atmospheric CO₂ and global greenhouse warming? *Geology* 21, 1059–1062.
- Velbel, M.A., 1993b. Formation of protective surface layers during silicate-mineral weathering under well-leached, oxidizing conditions. *Am. Mineral.* 78, 408–417.

- Velbel, M.A., 1995. Interaction of ecosystem processes and weathering processes. In: Trudgill, S.T. (Ed.), *Solute Modelling in Catchment Systems*. Wiley, New York, pp. 193–209 (Chapter 6).
- White, A.F., 2003. Natural weathering rates of silicate minerals. In: Holland, H.D., Turekian, K.K. (Ex. Eds), Drever, J.I. (Ed.), *Treatise on Geochemistry*, vol. 5, Surface and Ground Water, Weathering, and Soils, Elsevier, New York, pp. 133–168.
- White, A.F., Brantley, S.L., 1995. Chemical weathering rates of silicate minerals: an overview. In: White, A.F., Brantley, S.L. (Eds.), *Chemical weathering rates of silicate minerals, Reviews in Mineralogy*, vol. 31. Mineralogical Society of America, Washington, DC, pp. 1–22 (Chapter 1).
- White, A.F., Bullen, T.D., Vivit, D.V., Schulz, M.S., Clow, D.W., 1999. The role of disseminated calcite in the chemical weathering of granitoid rocks. *Geochim. Cosmochim. Acta* 63, 1939–1953.
- Yeakley, J.A., Swank, W.T., Swift, L.W., Hornberger, G.M., Shugart, H.H., 1998. Soil moisture gradients and controls on a southern Appalachian hillslope from drought through recharge. *Hydrol. Earth Syst. Sci.* 2, 41–49.