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Long-term average mineral weathering rates from watershed geochemical mass balance methods: Using mineral modal abundances to solve more equations in more unknowns

Jason R. Price [a,*], Noel Heitmann [b], Jennifer Hull [a], David Szymanski [c]

[a] Department of Earth Sciences, P.O. Box 1002, Millersville University, Millersville, PA 17551-0302, USA
[b] Department of Mathematics, P.O. Box 1002, Millersville University, Millersville, PA 17551-0302, USA
[c] Department of Geological Sciences, 206 Natural Science Building, Michigan State University, East Lansing, MI 48824-1115, USA

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ABSTRACT

The number of phases for which weathering rates can be determined by watershed geochemical mass balance is limited by the number of equations that can be constructed from elemental flux losses from the watershed and mineral stoichiometries. Mass balance studies of watershed weathering rates routinely use the flux losses of the six major cations SiO_2, Al, Na, K, Mg, and Ca. Analyses of these species in water are common, but following matrix algebraic methods limits the number of weathering rates that can be calculated to six.

For the Brubaker Run watershed located in the northern Piedmont Physiographic Province of Pennsylvania (USA), long-term (10^3–10^6 year) watershed chemical flux losses have been determined using ^{10}Be-derived total denudation rates and zirconium-normalized total chemical concentrations from bedrock and soils. Chemical flux losses calculated from solid-phase data have three advantages: They (1) Permit generation of a relatively large number of equations because both major and trace analyses are included; (2) eliminate the need for many years of regular (e.g., weekly) sampling and chemical analyses of stream water and atmospheric precipitation, and measurement of hydrologic parameters (i.e., precipitation, stream discharge, etc.); and (3) long-term weathering rate calculations need not address biomass.

For Brubaker Run, eight minerals are involved in weathering; the five primary minerals are REE-rich epidote, ankerite, almandine–spessartine garnet, muscovite, chlorite, and the three secondary products are weathered muscovite, kaolinite, and gibbsite. The long-term average weathering rates of these minerals were calculated using the six major cations, and two trace elements selected from Rb, Sr, Ba, La, Pr, Nd, Sm, Gd, and Dy. Despite having the eight equations needed, geochemically reasonable weathering rates (e.g., positive primary mineral rates that reflect destruction) could not be achieved regardless of the two trace elements used in the mass balance calculations. For Brubaker Run, this is primarily attributable to the natural heterogeneity of the trace element concentrations within the host mineral grains, with trace element stoichiometries in some minerals varying by as much as an order of magnitude. Because the trace elements are hosted by a relatively small number of minerals, the computed weathering rates of other minerals become very sensitive to small variations in trace cation stoichiometry.

REE-rich epidote, garnet, and ankerite within the Brubaker Run watershed together host nearly all of the Ca in the bedrock, and completely dissolve at or near the weathering front. Consequently, approximately all of the Ca in bedrock is lost from the regolith. In bedrock the mole-percentages of Ca hosted by REE-rich epidote, garnet, and ankerite are 49 mol%, 4 mol%, and 43 mol%, respectively, and are determined by the modal abundance of the mineral in the bedrock and its Ca stoichiometry. The weathering rates of REE-rich epidote, garnet, and ankerite can be determined by distributing to each mineral that fraction of the total watershed Ca flux loss for which it is responsible based on its mole-percent Ca in bedrock. By using a base cation that is completely lost from the regolith, and knowing the mole-percentage of that element in the mineral(s) undergoing weathering, additional equations may be added to the mass balance matrix. We term this technique the "flux distribution method." The flux distribution method eliminates the need for additional equations established using trace elements.

Based on the mineral weathering rates for the Brubaker Run watershed determined using the flux distribution method, the rates at which the weathering front penetrated the bedrock (the "saprolitization" rate) are 4.5 m Myr^{-1} and 6.5 m Myr^{-1} for chlorite and muscovite, respectively. These measured long-term

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[*] Correspondence author. Tel.: +1 717 872 3005; fax: +1 717 871 4725.
E-mail address: Jason.Price@millersville.edu (J.R. Price).

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average saprolitization rates compare very favorably with published theoretical values for the nearby northern Maryland Piedmont which range from 2.2 to 5.3 m Myr^{-1}.

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1. Introduction

Quantification of silicate mineral weathering is important as it is a natural mechanism by which atmospheric CO_2 is consumed over geologic time and hence has a significant impact on global climate (e.g., Walker et al., 1982; Berner et al., 1983; Berner, 1995; Berner and Kothavala, 2001). The chemical weathering of rocks also releases plant nutrients to soils (e.g., White and Brantley, 1995; Marschner, 1995; Brantley et al., 2005), and asserts a major influence on global geochemical cycles (Lasaga et al., 1994). Small watersheds are an important setting in which natural chemical weathering rates can be calculated (e.g., Berner and Berner, 1996). Geochemical mass balance methods applied to small watersheds are commonly used to calculate weathering rates of individual primary and secondary minerals in natural systems (e.g., Garrels, 1967; Garrels and Mackenzie, 1967; Velbel, 1985, 1986; Bowser and Jones, 2002; Bricker et al., 2003; Price et al., 2005a; Velbel and Price, 2007). Such 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). This approach employs a system of simultaneous linear equations with constant coefficients that represent the steady-state input–output behavior of the modeled systems (Velbel, 1986; Taylor and Velbel, 1991; Velbel and Price, 2007). A fundamental limitation of watershed mass balance calculations is that they may involve more unknowns (the rates of weathering of individual primary minerals and/or the rates of formation of secondary minerals) than equations (the number of elements for which stream solute flux data are available) (e.g., Finley and Drever, 1997; Bowser and Jones, 2002; Bricker et al., 2003; Velbel and Price, 2007). Under such circumstances, the system of linear equations will not yield a unique solution (Finley and Drever, 1997; Bowser and Jones, 2002; Bricker et al., 2003; Velbel and Price, 2007). The purpose of this paper is to introduce a simple method for overcoming the problem of unknowns exceeding equations in watershed mass balance studies; we term this technique the "flux distribution method". Rather than relying on analyses of additional chemical species in stream water (i.e., yielding additional equations), we propose establishing weathering rate constraints based on the bedrock mole-percentage of a base cation in a weathering mineral. For application of this method the base cation utilized must be completely lost, or nearly so, from the regolith during weathering.

Watershed mass balance studies to date (e.g., Garrels, 1967; Garrels and Mackenzie, 1967; Velbel, 1985, 1986; Bowser and Jones, 2002; Bricker et al., 2003; Price et al., 2005a; Velbel and Price, 2007) calculate watershed regolith elemental flux losses by multiplying stream discharge by the elemental concentration of the stream water, and dividing by watershed area (e.g., units of mol ha^{-1} yr^{-1}; Creasey et al., 1986). From these flux loss values the elemental flux into the watershed (from precipitation amounts and chemistry; e.g., Swift et al., 1988) is subtracted, yielding the flux losses attributable to chemical weathering. Ideally, the hydrologic data is measured continuously (or at short regular intervals) and the precipitation and stream water chemistry is based on samples collected weekly for a minimum seven-year record (e.g., Swank and Waide, 1988; Likens and Bormann, 1995). It should be recognized that such data sets only reflect the present-day interglacial environmental conditions (e.g., climate, geomorphology) for the period of record, and may or may not reflect geochemical changes occurring on geologic (10^3–10^6 year) timescales (e.g., White, 2003).

This study differs from traditional watershed geochemical mass balance studies in that the elemental flux losses from the watershed have been calculated using ^{10}Be-derived total denudation rates and zirconium-normalized total chemical concentrations in both bedrock and soils (methods of Riebe et al., 2001, 2003, 2004a,b). The advantages of doing so are four-fold: (1) Mineral weathering rates calculated from the elemental fluxes reflect chemical weathering on geologic timescales; (2) biomass does not need to be addressed in the calculations of geologic timescale chemical weathering rates because biological processes operate on short-term (years to centuries) timescales (Drever, 1997); (3) the elemental flux losses are calculated from a one-time sample episode of soil and bedrock, rather than many years of weekly precipitation and stream water sampling in conjunction with hydrologic measurements; and (4) ten or more major and trace element fluxes can be easily calculated from bulk chemical data generated using X-ray fluorescence spectroscopy (XRF). XRF data may also be used in conjunction with more sensitive instrumentation suitable for trace element analyses such as laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). Elemental stream flux data are often limited to the five major elements SiO_2, K, Na, Mg, and Ca. A sixth stream flux may be added by assuming a negligible Al flux, but still yielding an insufficient number of equations to calculate seven or more mineral weathering rates.

2. Background

2.1. Previous work

Velbel and Price (2007) provide a thorough review of previous approaches used in attempting to overcome the limitation of having more unknowns than equations in watershed mass balance calculations of mineral weathering rates. A brief summary is provided below.

For watershed mass balance studies using present-day stream solute elemental fluxes, one way to eliminate an unknown is to exclude a biomass term (e.g., Afifi and Bricker, 1983; Bowser and Jones, 2002; Bricker et al., 2003). However, excluding biomass is only valid if the growth of new vegetation is exactly balanced by the death and decay of old vegetation, which is rarely true (e.g., Taylor and Velbel, 1991; Likens and Bormann, 1995; Velbel, 1995; Drever, 1997; Bricker et al., 2003).

The number of unknowns in watershed mass balance calculations may also be reduced by "coupling" primary and secondary phases. Coupling refers to the clay formation rate being calculated from its stoichiometric relationship with the weathering rate of a primary mineral. For example, Velbel (1985) and Taylor and Velbel (1991) coupled biotite weathering and vermiculite transformation by assuming conservation of the silicate sheet. In this scenario, the weathering rate of biotite would equal the formation rate of vermiculite. A similar relationship may also be established for plagioclase and kaolinite (or gibbsite), assuming conservation of aluminum. The disadvantage of coupling is that the results of the mass balance will not be permitted to reflect the decomposition of the secondary mineral and formation of a tertiary (or quaternary) phase and solutes (Velbel and Price, 2007). Furthermore, the relationship between primary and secondary minerals is often sufficiently complicated that a secondary phase cannot be linked to only one primary phase, and vice versa.

Bowser and Jones (2002) and Bricker et al. (2003) introduced the idea of the "fictive phase". A fictive phase is defined 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