

GEOCHEMICAL MASS BALANCES AND WEATHERING RATES IN FORESTED WATERSHEDS OF THE SOUTHERN BLUE RIDGE*

MICHAEL ANTHONY VELBEL

Department of Geology and Geophysics,
Yale University**

ABSTRACT. Weathering rates of rock-forming silicate minerals in natural forested watersheds can be calculated using a system of geochemical mass balance equations constructed and constrained by petrologic, mineralogic, hydrologic, botanical, and aqueous geochemical data. Solving the systems of equations for the weathering rates of biotite mica, almandine garnet, and oligoclase-andesine plagioclase feldspar in deeply weathered (sapolitized) schists and gneisses of a study area (the USDAFS Coweeta Hydrologic Laboratory, near Otto, N.C.) suggests that: (1) The rate at which the weathering front penetrates into the fresh rock (3.8 cm/1000 yrs) agrees well with the "average" denudation rate for the southern Appalachians (4 cm/1000 yrs) determined by a variety of different methods. (2) When normalized to the estimated mineral surface area in the watersheds, rates of garnet and plagioclase weathering are approximately one to two orders of magnitude slower than rates determined in laboratory experiments under similar hydrogeochemical conditions. Two possible sources of this discrepancy are (A) the character of artificially-treated mineral surfaces, which renders them more reactive than their natural counterparts, and/or (B) difficulties in estimating reactive mineral surface area in natural systems. (3) Present rates of primary mineral weathering and secondary mineral neoformation at Coweeta appear to be sufficient to neutralize present levels of atmospheric hydrogen ion input. The relatively good accord between field and laboratory geochemical and geomorphologic results suggests that present sources of error *may* not be large, that mass-balance models provide quantitative estimates of rates of important environmental processes, and that refinement of laboratory kinetic data and field surface area determinations should rank high among future research priorities.

INTRODUCTION

A tremendous literature on kinetics of mineral dissolution in the laboratory exists. To date, however, studies of mineral weathering kinetics in nature have been less numerous. Most geochemical research on natural weathering has been oriented toward explanations of the chemical composition of soil- and groundwaters that drain areas of active rock-water interactions. Some notable examples are Feth, Roberson, and Polzer (1964), Garrels (1967), Garrels and Mackenzie (1967), Bricker, Godfrey, and Cleaves (1968), Helgeson, Garrels, and Mackenzie (1969), Cleaves,

* Paper presented at American Geophysical Union session *Geochemistry/Water Quality of Catchments*, Cincinnati, Ohio, May, 1984, and NATO Advanced Research Workshop *The Chemistry of Weathering*, Rodez, France, July, 1984.

** Current address: Department of Geological Sciences, Michigan State University, Lansing, Michigan 48824-1115

Godfrey, and Bricker (1970), Cleaves, Fisher, and Bricker (1974), Drever (1971), Marchand (1971, 1974), Fritz (1975), and Pačes (1978). These studies attempted to interpret the composition of groundwater (and resulting streamwater) in terms of chemical reactions between parent minerals and weathering products in near-surface weathering environments. The studies suggest or necessarily assume that soil- and groundwaters are in equilibrium with observed or inferred weathering products or with hypothetical metastable phases. However, a study undertaken in the Absaroka Mountains by Miller and Drever (1977) has demonstrated that stream waters there are not in equilibrium with weathering products found in the nearby soil. Miller and Drever suggest, after Pačes (1973, 1976), that these waters reflect deep incipient alteration of large volumes of rock and that the composition of deep weathering waters is controlled not by equilibrium with weathering products, but by the relative rates of dissolution, precipitation, and water movement through the deep weathering zone. This represents a significant departure from the mainstream of much past geochemical thought on chemical weathering, both in its emphasis on non-equilibrium (kinetic) factors and in its emphasis on the deep sub-soil portion of the weathering profile.

The theoretical literature on geochemical kinetics in natural silicate-weathering systems is small but growing (Pačes, 1973, 1976, 1978; Berner, 1978, 1981; Lasaga, 1981a, b, c, 1984), but relatively little has been done to relate laboratory kinetic data to natural weathering situations, with a few exceptions (Claassen and White, 1979; White and Claassen, 1980; White, Claassen, and Benson, 1980; Pačes, 1983; Siegel, 1984). The purpose of this paper is to calculate rates of mineral weathering in the natural environment using a refined geochemical mass-balance model. Rates calculated for natural weathering are then compared with rates determined in laboratory studies and with other theoretical and observational work on rates and mechanisms of rock and mineral weathering.

Mass-balance studies are widely considered the most reliable means for making quantitative determinations of elemental transfer rates in the Earth's surface environment (Clayton, 1979). Studies of watershed geochemical mass-balances (input-output budget models) were largely developed and implemented by Garrels (1967; Garrels and Mackenzie, 1967) and Cleaves and Bricker (Bricker, Godfrey, and Cleaves, 1968; Cleaves, Godfrey, and Bricker, 1970; Cleaves, Fisher, and Bricker, 1974). The following discussion is based on their work.

Garrels' work involved modeling changes in solution *concentration*, giving results with units of moles of mineral reaction per liter of water. Cleaves and his coworkers modeled changes in solute *fluxes* (determined by measuring concentrations and flow rates over the study period); their results are expressed as mass of mineral reaction (number of moles of a stoichiometric weathering reaction) per acre of watershed per duration of the study (equivalent to moles of reaction per area of watershed per time, for example, years). Cleaves, Godfrey, and Bricker (1970) were thereby able to calculate chemical weathering rates for the landscape

and the weathering rates of individual minerals in the weathering profiles of their study area.

Cleaves, Godfrey, and Bricker (1970) recognized that weathering reactions in a forested watershed produce larger quantities of mineral nutrients (especially calcium and potassium) than are observed in streams, and that these excess quantities are probably taken up by the forest biota. Likens and others (1977) also recognized that weathering products derived from the breakdown of soil minerals leave the weathering profile both *via* streams and *via* biomass uptake, and that estimates of weathering rates (that is, mineral breakdown rates) based only on stream fluxes might be as much a factor of two lower than the actual value which includes biotic uptake.

The model developed herein extends previous studies of geochemical mass balances in two ways. First, in contrast to the studies cited above, in which mineral compositions and reaction stoichiometries were assumed to be nearly ideal (essentially estimated from geological occurrence and standard mineralogy texts), mineral compositions in this study were determined empirically, and compositional data were combined with petrographic (micromorphological) data to arrive at the mineral weathering reactions used in the mass-balance equations. Secondly, botanical uptake of three major mineral nutrients (potassium, calcium, and magnesium) is explicitly included in the mass-balance expressions, permitting biomass uptake to be solved directly rather than by difference.

In this investigation coexisting saprolites and streamwater have been studied in a small area (of known climate) in the southern Appalachians, the Coweeta Hydrologic Laboratory of the U.S. Department of Agriculture Forest Service. To minimize the influence of biomass state on the mineral nutrient budgets (for example, Likens and others, 1977), emphasis, in this study, is placed on control (undisturbed) watersheds as much as possible. Watersheds were chosen for detailed study on the basis of management history, amount of hydrogeochemical data available from the Forest Service, bedrock type, mean annual discharge, and proximity to pre-existing cores and wells. Major characteristics of the study watersheds are summarized in table 1. Emphasis is placed on deep saprolites (C horizon), rather than surficial soils, in order both to minimize problems associated with biological processes such as bioturbation, aluminum and iron chelation by organic acids, and biogeochemical cycling of nutrients (for example, see Likens and others, 1977; Graustein, 1976, 1981), and to provide material that has weathered in place, thereby inheriting the original textures of the parent rock. The saprolite accounts for some 95 percent (5.8 m; 19 ft) of the thickness of the average weathering profile at Coweeta (6.1 m; 20 ft — Berry, 1976, Douglass and Swank, 1975).

The term “saprolite” was proposed by Becker (1895) “as a general name for thoroughly decomposed, earthy, but untransported rock.” Over the years the definition has come to mean a residual soil developed on crystalline rocks in which some or all of the primary minerals have been extensively transformed *in situ* to weathering products. The weathering

products are usually pseudomorphous after the parent minerals, resulting in the preservation of rock textures, fabrics, and structures in the saprolite. Preservation of parent rock textures permits positive identification of parent material and provides a framework against which the spatial redistribution of the constituents of solid weathering products can be measured. This greatly simplifies the interpretation of alteration textures.

THE STUDY AREA

At first the earth was flat and very soft and wet. The animals were anxious to get down, and sent out different birds to see if it was dry yet, but they found no place to alight and came back again to Galunlati. At last it seemed to be time, and they sent out the Buzzard and told him to go and make ready for them. This was the Great Buzzard, the father of all the buzzards we see now. He flew all over the earth, low down near the ground, and it was still soft. When he reached the Cherokee country, he was very tired, and his wings began to slap and strike the ground, and wherever they struck the earth there was a valley, and where they turned up again there was a mountain. When the animals above saw this, they were afraid that the whole world would be mountains, so they called him back, but the Cherokee country remains full of mountains to this day.

Cherokee Origin Myth (Mooney, 1900)

The Coweeta Hydrologic Laboratory of the U.S. Forest Service is located in the Nantahala Mountains 15 km (10 miles) southwest of Franklin, N.C. The laboratory area comprises approximately the southeast quarter of the U.S. Geol. Survey Prentiss, N.C., 7½' quadr. (fig. 1).

Topography and climate.—The physiographic Coweeta Basin totals some 1625 hectares, ranging in altitude from over 1585 m (5200 ft) at its western limit to about 670 m (2200 ft) in the valley of Coweeta Creek in the east. Slopes within individual watersheds average about 45 percent

TABLE 1
Summary of important characteristics of Coweeta watersheds

Watershed no.	Rock type*	Discharge**	Cores available	Management summary	Water data***	Sampled for this study?
2	TF	1.09	—	Control	P,L,S	Yes
14	CG/TF	1.40	C5(TF)	Control	P,S	Yes
18	TF	1.25	—	Control	P,S	Yes
27	CG	2.10	C9,C15	Control†	P,L,S	Yes
32	CG	1.82	—	Control	P,S	No
34	TF	1.52	—	Control	P,S	No
36	TF/CG	2.06	C17	Control	P,S	No

* Dominant rock type. Where two are present in subequal amounts, both are indicated, with areally dominant shown first.

TF — Tallulah Falls Formation

CG — Coweeta Group

** Area meters

*** P — Precipitation chemistry from Swank and Douglass (1977)

S — Stream chemistry from Swank and Douglass (1977)

L — Lysimeter data from Coweeta archives (unpub.)

W — Well data from Coweeta archives (unpub.)

† Control watershed recovering from partial defoliation by infestation by fall cankerworm.

Rock type from Hatcher (1980), cores from Berry (1976; samples courtesy of John L. Berry and the Coweeta Hydrologic Laboratory), all other data from Swank and Douglass (1977).

(27°). Average annual rainfall is among the highest in eastern North America, ranging from 170 cm (80 in.) at lower elevations to 250 cm (100 in.) on the upper slopes; this corresponds roughly to decreasing rainfall with distance east from the western boundary of the Laboratory. Less than 5 percent of the annual precipitation falls as snow. The mean annual temperature is 12.8° Celsius (55°F); average maxima and minima are 33°C (92°F) and -17°C (1°F), respectively. Physiographic and climatic data are from Swank and Douglass (1975), Douglass and Swank (1975), and Hewlett and Douglass (1968).

The area was occupied by Cherokee Indians until the appearance of white settlers in 1842 (Johnson and Swank, 1973). "Contrary to popular opinion, many parts of the Southeast were not virgin forest when Europeans first arrived. The Indians actually modified the forest cover far out of proportions to their numbers. They repeatedly burned off large portions of the forest to create grazing lands, artificially stimulating the number of deer" (Hudson, 1976). Most of this sort of environmental manipulation occurred in the Piedmont, however (Hudson, 1976); Cher-

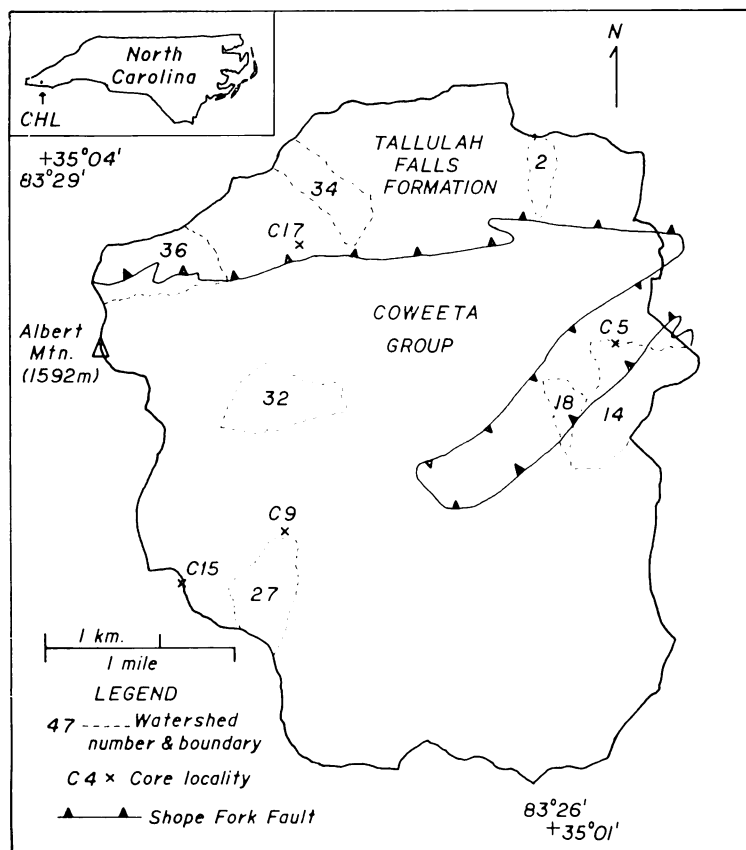


Fig. 1. Map of the Coweeta Hydrologic Laboratory.

oaks in the Appalachian Summit region did not apparently alter their environment to the same extent (Keel, 1976). From 1909 to 1923, controlled selection logging was conducted in valleys and more accessible lower slopes. No fires or cutting operations have been conducted in control watersheds since the Forest Service acquired all rights to the area in 1924 (Johnson and Swank, 1973). *Quercus* (oak) species, *Carya* species, and red maple (*Acer rubrum* L) dominate the multistoried hardwood stand (Johnson and Swank, 1973; Douglass and Swank, 1975; Swank and Douglass, 1975).

Bedrock geology.—Two major lithostratigraphic units occur in the study area. The Tallulah Falls Formation (Hatcher, 1971) consists of metagraywackes, pelitic schists, and metavolcanic rocks, derived mainly from sedimentary protoliths of low mineralogical maturity (for example, graywackes). The Coweeta Group (Hatcher, 1974, 1979) consists of biotite gneisses, metaarkoses, metasandstones, quartzites, and pelitic and biotite schists, which were derived predominantly from sedimentary protoliths of intermediate to high mineralogical maturity (for example, arkoses, quartzarenites). Similar assemblages of rock-forming minerals characterize both units. Major minerals present are quartz, muscovite and biotite micas, plagioclase feldspar, and almandine garnet; accessory minerals include chlorite, kyanite, epidote, clinozoisite, magnetite, staurolite, sillimanite, and, locally, microcline, hornblende, zircon, apatite, sphene, and tourmaline (Hatcher, 1976, 1979). One small watershed (#3) is underlain by plagioclase-hornblende rocks of the Carrol Knob Mafic Complex (Hatcher, 1980).

The older Tallulah Falls Formation was thrust eastward over the younger Coweeta Group rocks along the Shope Fork Fault (Hatcher, 1976, 1978; fig. 1). Amphibolite-facies metamorphism associated with the Ordovician Taconic Orogeny created the mineral assemblages outlined above (Hatcher, 1976, 1979; Hatcher and Butler, 1979). For the purposes of this study, the qualitative difference between the two main lithostratigraphic units must suffice; the heterogeneity of rock types, combined with the extreme structural complexity of the area, makes it exceedingly difficult to estimate quantitatively the absolute or relative abundance of the different minerals and rock types. Some (hydrothermal?) alteration, probably synmetamorphic, affected rocks near the Shope Fork Fault. All rocks, and the Shope Fork Fault, were then folded about northeast-trending fold axes, creating the Coweeta Syncline and determining the present outcrop pattern (Hatcher, 1979, 1980; fig. 1).

There is another world under this, and it is like ours in everything — animals, plants, and people — save that the seasons are different. The streams that come down from the mountains are the trails by which we reach this underworld, and the springs at their heads are the doorways by which we enter it, but to do this one must fast and go to water and have one of the underground people for a guide. We know that the seasons in the underworld are different from ours, because the water in the springs is always warmer in winter and cooler in summer than the outer air.

Hydrology.—As its name implies, the Coweeta Hydrologic Laboratory is a major focus of hydrologic research. Nutrient cycling research was added to the research repertoire in 1968 (Monk and others, 1977). Although an overview of the important findings made at Coweeta is beyond the scope of this review, several hydrologic findings of the ongoing research bear directly on this study.

Base flow is apparently sustained by prolonged drainage of moist but unsaturated soil and saprolite (Hewlett, 1961; Hewlett and Hibbert, 1963). During the “hydrologic survey” of Coweeta in the early 1930’s, 28 wells were dug to bedrock (by hand) to depths of 1.5 to 11 m (5–35 ft); regolith depth at Coweeta averages around 6.1 m (20 ft; Douglass and Swank, 1975; Swank and Douglass, 1975). When pumped dry, 21 failed to recover until heavy rains occurred. From this behavior, it was concluded that water in these wells reflected “cistern” storage rather than water levels in an areally extensive aquifer. The remaining 7 wells were located near stream channels or in mountain flood plains and may be connected to local bodies of “groundwater.” Hewlett (1961) concluded that a saturated groundwater-table-like aquifer does not exist to supply base flow to Coweeta streams. Hewlett (1961) also presented and discussed evidence that fissures in the bedrock are also not major sources of base flow.

In a simple and elegant experiment designed to test a hypothetical source of base flow, Hewlett (1961) and Hewlett and Hibbert (1963) constructed giant concrete troughs, which were filled with “subsoil” (C horizon soil), packed to approximately its natural bulk density; moisture tensiometers and neutron-scattering probes were emplaced, as was a “spigot” at the lower end. The experimental hillslopes were then saturated with water to simulate intense precipitation, covered to prevent evaporation, and permitted to drain under the influence of gravity. The results suggested that drainage continued long after the pores became unsaturated, and that the unsaturated soil zone could contribute sufficient water to sustain observed rates of base flow even after 60 days without recharge. Recharge is usually much more frequent at Coweeta than in the experiment. Hewlett concluded that prolonged drainage of unsaturated pores is the primary source of base flow to Coweeta streams. There is no evidence that the mountain streams of Coweeta are fed by water from the permanently-saturated water-table.

Storm flow at Coweeta is also dominated by drainage in the unsaturated zone. Hewlett and Hibbert (1966) attribute the “flashy” response of Coweeta streams to storms as a result of “subsurface translatory flow, or the rapid displacement of stored water by new rain” (p. 275). “Above the zone of saturation, we may regard such movement as due to thickening of the water films surrounding soil particles and a resulting pulse in water flux as the saturated zone is approached. The process under rainfall is varying everywhere in a most complex way, but such movement can be verified in an elementary manner by allowing a soil column to drain to field capacity in the laboratory and slowly adding a unit of water at the top. Some water will flow from the bottom almost immediately, but it

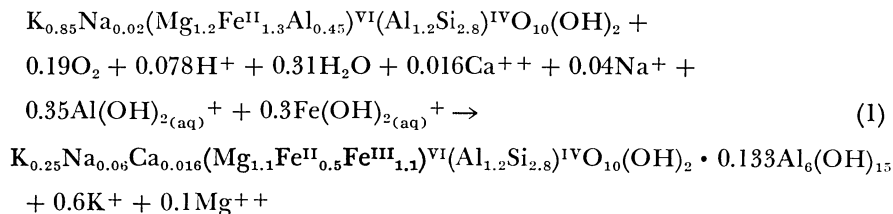
will be apparent that it is not the same water added at the top" (p. 279). Hewlett and Hibbert (1966) cite experimental work using tritium-labelled water (Horton and Hawkins, 1964) to support this notion. Horton and Hawkins found that 87 percent of the water originally held in pores was "pushed" out of the soil by a plug of tritium-tagged water before any tritium appeared in the effluent. High-runoff episodes therefore involve "the rapid displacement of stored water by new rain" rather than interflow or overland flow. Observations on hydrogen, oxygen, and radon isotopes in natural systems led Sklash and Farnvolden (1982) to the same conclusion regarding the major contribution of subsurface water in high-runoff episodes. Winner (1977) determined that similar subsurface flow characteristics probably apply to much of the North Carolina Blue Ridge.

A large body of observation, experiment, and theory, based on work at Coweeta and elsewhere, suggests that both base flow and storm flow are sustained by water from depth in the subsurface (saprolite), and that neither overland flow nor interflow contributes directly (or significantly) to the streams.

MINERAL WEATHERING REACTIONS

The transformation of rock to saprolite at Coweeta is primarily due to the weathering of three minerals: biotite mica, almandine garnet, and sodic plagioclase feldspar. Other major rock-forming minerals are present in abundances too small to affect major-element budgets or are not detectably weathered.

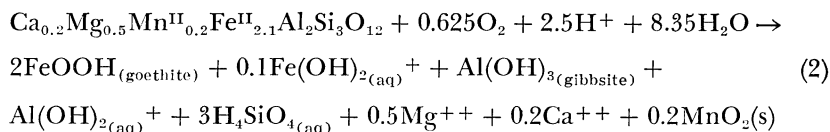
Biotite weathers by a mechanism in which the primary phyllosilicate lattice is conserved; compositional change during weathering is due largely to removal and partial replacement of interlayer cations, with minor changes in octahedral sites (Velbel, 1984a and in preparation). The main weathering product in saprolite is hydrobiotite, a regularly-interstratified biotite-vermiculite (Velbel, 1984a and in preparation). Continued weathering in soils produces vermiculite and/or "pedogenic chlorite." The stoichiometric expression for the biotite weathering reaction, based on the aforementioned constraints and electron probe microanalysis (EPMA; Velbel, in preparation) is¹:



¹ In this and all other reactions, dissolved species were determined on the following bases: (1) Alkali and alkaline earth species in the very-low-ionic-strength waters of Coweeta were estimated by the method of Berner (1971), and complexation was found to be negligible. (2) Fe and Al species chosen are those that dominate in the pH range (~5-6; Velbel, 1985, table 1) of Coweeta soil and subsurface solutions; speciation data used are those of Lindsay (1979) and Drever (1982).

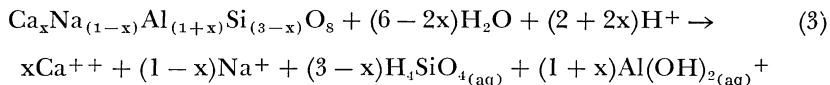
The weathering of biotite to hydrobiotite releases a significant proportion of the potassium and some of the magnesium present in the parent mineral and results in the removal of a small amount of calcium and sodium from the ambient soil- or groundwater.

Almandine garnet in saprolite is transformed by congruent breakdown of the parent garnet, localized reprecipitation of most of the iron (as goethite) and some of the aluminum (as gibbsite), and removal of the remaining constituents in solution (Velbel, 1984b). The gibbsite-goethite layer which forms in the saprolite is apparently a protective surface layer, governing reaction rates by limiting the rate of reactant and/or product transport (Velbel, 1984b). Organic chelating agents in soils prevent the localized precipitation of iron and aluminum, and all constituents are removed from the garnet microenvironment, leaving unprotected garnet surfaces which are vulnerable to surface-controlled weathering reactions (Velbel, 1984b). The garnet weathering reaction for Tallulah Falls Formation rocks can thus be written as:



Garnet in the Coweeta Group has about half the calcium of Tallulah Falls garnet. The weathering of almandine contributes significant quantities of silica, calcium, and magnesium to the soil and groundwaters.

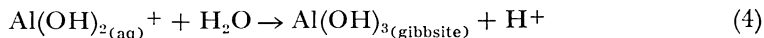
Plagioclase feldspar weathers by selective attack at defects in the lattice (a surface-controlled reaction), which are often more abundant in one set of albite twin-lamellae than in the other (Velbel, 1983). The weathering of plagioclase feldspar at Coweeta is a two-step process. Dissolution voids (vacuoles, etch pits) are usually empty in early stages of weathering, indicating that the dissolved constituents derived from the congruent breakdown of the primary feldspar lattice are removed from the loci of weathering and reprecipitated elsewhere from the ambient solution (Velbel, 1983). Feldspar weathers according to the reaction:



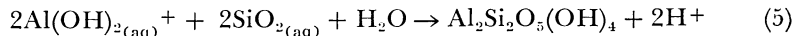
where $x = 0.25$ for rocks of the Coweeta Group and $x = 0.32$ for rocks of the Tallulah Falls Formation (determined by EPMA).

The second stage of the plagioclase weathering reaction is the precipitation of some of the dissolved constituents (released by the dissolution of the feldspar in the first stage of the reaction) as clay minerals, which may occur either very close to the original site of dissolution (forming clay-mineral pseudomorphs after the feldspar) or after transport (as clay-mineral fracture-linings) some microns to millimeters or more from the original site of dissolution (Velbel, 1982, 1983, in preparation). The clay-mineral products of plagioclase feldspar weathering in the soils and

saprolites of Coweeta are gibbsite and kaolinite, which precipitate by reactions:



and



The presence of these cation-depleted clay minerals in the saprolites of Coweeta could indicate either prolonged weathering (that is, that the weathering profile of Coweeta is extremely old) or very intense weathering over a shorter time scale, with the relative depletion of alkali and alkaline earth cations due to extremely rapid flushing of water through the weathering profile. Given the extremely high rainfall and the persistence of primary rock-forming minerals in the soils and saprolite of Coweeta, it appears that the kaolinite–gibbsite mineralogy of the soils and saprolites is due more to the intensity of weathering at Coweeta than to the antiquity of the weathering profile (Velbel, 1982, 1983, 1985, in preparation). As is discussed below, present day rates of mineral and chemical weathering of Coweeta rocks could produce the observed thickness of saprolite in several hundred thousand years, suggesting that the Coweeta landscape may be much younger than many kaolinitic–gibbsitic landscapes beneath multi-million year-old “peneplains.” Other clay minerals form in incipiently weathered bedrock below the saprolite and in outcrop, but as is shown in the section on hydrology (above), these subsaprolite weathering microenvironments involve minimal quantities of the subsurface water relative to the saprolite (which contributes the bulk of the streamflow) and therefore do not contribute measurably to the dissolved load of surface or subsurface waters.

Most streamflow at Coweeta is fed by subsurface water percolating through the soil and saprolite (for example, Hewlett and Hibbert, 1966); as a consequence, only the weathering reactions taking place within the soil and saprolite influence the composition of streamwaters leaving Coweeta watersheds. The close correspondence between the geochemical character of the streamwaters and the clay mineralogy of the saprolite (as opposed to the incipiently weathered bedrock; Velbel, 1982, 1985, in preparation) is consistent with what is presently known regarding the importance of saprolite as the principal source of stream flow at Coweeta (see section on hydrology, above). The amount of water percolating into and through fractures in the bedrock is apparently extremely small relative to the amount flowing through the saprolite, and mineral-water interactions taking place within these small bedrock fractures leave no detectable imprint on the geochemistry of Coweeta waters. Because only mineral transformations taking place within the soil and saprolite influence the measured output fluxes *via* Coweeta streams, only these reactions need to be considered in geochemical modeling of input-output budgets in small watersheds, and the reactions taking place within the bedrock are quantitatively insignificant.

GEOCHEMICAL MASS BALANCE

The total standing stock of “available dissolved nutrient” in a forested watershed (the “mineral nutrient reservoir” of fig. 2) can be augmented and depleted in a number of ways. Atmospheric precipitation can add nutrients, as can the weathering of primary minerals. The formation of weathering products removes elements, possibly including nutrient elements; plant growth can remove nutrients, and elements can be permanently removed from the watershed in the dissolved load of streams. A net accumulation of soil moisture or groundwater would represent an additional budgetary output for elements, as would subsurface leakage out of the watershed, whereas net depletion of subsurface water (which would presumably ultimately appear as stream discharge, if the basin is hydrologically “tight”) would have to be treated as an additional input term to the overall hydrogeochemical budget.

For the purposes of this study, the control watersheds of Coweeta are considered to be at steady-state. This is probably a safe approximation. The dissolved flux data of Swank and Douglass (1977), which are used in making all the following calculations, span a time interval of 4 to 7 yrs for the alkalis and alkaline earths. This is sufficiently long that it reflects a reasonable average of seasonal and annual variations (Likens and others, 1977), yet short enough that long-term ecological or climatological trends have not had an appreciable effect. (This does not mean, necessarily, that the biomass is fixed, only that its rate of nutrient uptake, that is, “growth,” has not changed appreciably over the duration of the data acquisition period). See Velbel (1985) for a detailed discussion of the hydrogeochemical data used in this study.

Chloride is approximately in balance in all watersheds (Swank and Douglass, 1977), so groundwater storage, depletion, or leakage are negligibly small and can therefore be ignored for the remainder of this study.

Because precipitation input and stream output fluxes are known from Swank and Douglass (1977), and “groundwater” change or losses are

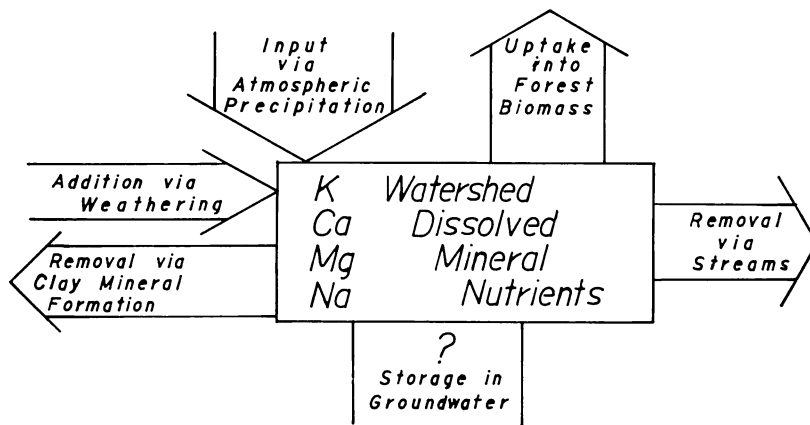


Fig. 2. Diagrammatic watershed mass balance model (see text for discussion).

negligible, only six sources and sinks must be determined by mass balance modeling; three primary-mineral weathering reactions (plagioclase, garnet, and biotite; reactions 1 to 3); two clay-mineral neoformation reactions (gibbsite and kaolinite, reactions 4 and 5), and biomass uptake. Neoformation of smectite in incipiently weathered bedrock is insignificant, because only a small fraction of the water passing through a watershed is ever involved in smectite-forming reactions, and this small quantity of water does not appreciably affect stream flow or solute budgets (Velbel, 1982, 1985, and in preparation). Also, none of the major mineral nutrients (potassium, calcium, magnesium) or sodium is consumed by the formation of gibbsite or kaolinite. As a consequence, only four source or sink terms affect potassium, calcium, magnesium, and sodium.

Following the formalism of Plummer and Back (1980), the mass-balance relations can be summarized as follows:

$$\begin{aligned} \phi \\ \sum_{j=1} \alpha_j \beta_{c,j} = \Delta m_c \quad (6) \\ c = 1 \dots n \end{aligned}$$

Where $\beta_{c,j}$ is the stoichiometric coefficient of element c in reaction j (units are moles of c per mole of weathering reaction j , except for biomass for which units are moles of c per kilogram of annual "new growth" biomass; positive for products, negative for reactants); Δm_c is the net flux of element c (stream output minus rain input), from Swank and Douglass (1977) expressed as moles/ha/yr, positive for net efflux; and α_j is the number of moles of weathering reaction j (or kilograms of biomass growth) which occurs per hectare per yr, positive when reactions 1 to 3 proceed forward as written, and when biomass is produced.

For the three mineral weathering reactions, all stoichiometric coefficients are known from petrographic and mineralogical analysis (Velbel, 1982, 1983, 1984a, b, 1985, and in preparation). The "stoichiometry" of calcium, potassium, and magnesium uptake by biomass can be determined from the data of Day (from Day and Monk, 1977), as reproduced in Boring, Monk, and Swank (1981). Sodium is taken up in small quantities by biomass (Likens and others, 1977), but to a much lesser extent than the other three cations; in the absence of biomass data for sodium at Coweeta, it is assumed that biomass is not a sink for sodium.

Eq 6 now represents a system of $n = 4$ equations (the mass balances for K, Ca, Mg, and Na) in $\phi = 4$ unknowns (the number of moles of plagioclase, garnet, and biotite weathered, and the kilograms of biomass "growth," all per hectare per yr); all 16 stoichiometric coefficients are known. Eqs 6 were solved algebraically, and the result coded in BASIC for microcomputer use; the algebraic result was verified by use of a standard linear-algebra matrix-solving routine. Weathering rates of plagioclase, biotite, and garnet, and the rate of biomass "uptake" of mineral nutrients, were calculated for seven Coweeta control watersheds (including both those studied in detail, and others that are lithologically similar), four

on Tallulah Falls Formation rocks and three on Coweeta Group rocks, assuming that the biomass composition is identical for all seven. Mineral weathering rates are plotted as a function of long-term average discharge in figure 3.

It is apparent from figure 3 that the calculated rates of plagioclase and biotite weathering vary between rock types, whereas the garnet weathering rate is largely independent of rock type. Furthermore, these differences are not merely artifacts of using different plagioclase and garnet compositions for the two rock types; a test set of calculations determined that, even if there were no differences in mineral composition between the two rock types, plagioclase and biotite weathering rates in Coweeta Group watersheds would still be lower than those for Tallulah Falls watersheds. The mass-balance calculations strongly suggest that there is "more" feldspar and biotite weathering in Tallulah Falls rock than Coweeta Group rocks. Either comparable amounts of both minerals weather more quickly in Tallulah Falls than in Coweeta Group watersheds, or, more likely, there is just more plagioclase and biotite in the Tallulah Falls than in the Coweeta Group, weathering at comparable rates, precisely as would be expected given what is known about the comparative lithology of the two rock types. This is entirely consistent with the observations and speculations of Swank and Douglass (1977) regarding elemental concentrations in streams as a function of rock type.

RATE OF SAPROLITE FORMATION

Modal analysis gives the volume of a given mineral per unit volume of rock; the molar volume permits us to estimate how much primary mineral (by volume) is weathered per hectare per yr, by using the rates determined from geochemical mass-balance calculations. The amount of time required to convert a unit volume of rock to saprolite (that is, the amount of time required completely to weather a given primary mineral out of a volume of rock) is therefore easily obtained.

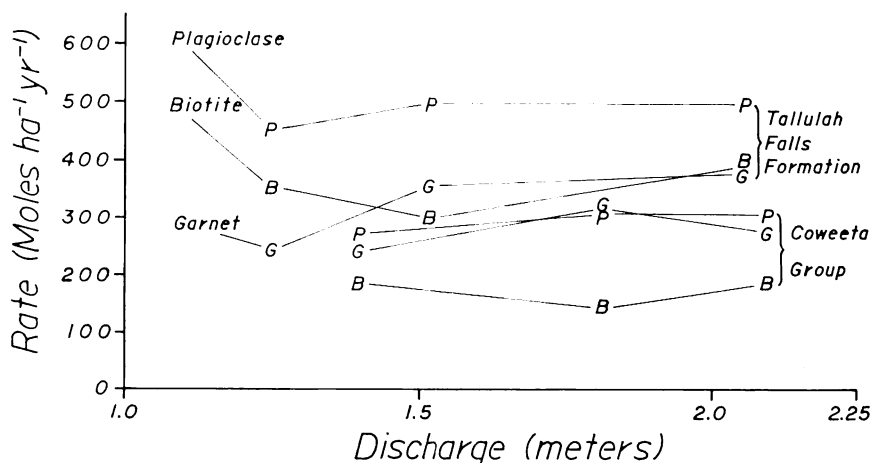


Fig. 3. Mineral weathering rates *versus* discharge.

TABLE 2
Modal petrography of Coweeta Group Rocks
Watershed 27 (N=18)

Quartz	61.6
Biotite	11.6
Garnet	1.9
Muscovite	12.9
Plagioclase	8.3
Opauques	1.4
Epidote	.1
Staurolite	.9
K-spar?	.6

Watershed 27 and two nearby cores were chosen for much of the following analysis for two reasons: First, the two cores permit better two-dimensional control (that is, more samples from depth to complement the outcrop samples): second, watershed 27 is the farthest removed from the Shope Fork Fault and its associated alteration, making it the best for modal petrographic analysis of unaltered Coweeta Group rocks. Petrographic analyses of 18 Coweeta Group samples from watershed 27 and cores 9 and 15 are summarized in table 2.

At the present rate of weathering, it would take about 40,000 yrs to deplete 6.1 m (20 ft) of rock of all of its garnet, 140,000 yrs to transform all biotite to hydrobiotite, and 160,000 yrs to weather all the oligoclase. A time scale of around 100,000 yrs is all that is required to transform 6.1 m (20 ft) of rock to 6.1 m (20 ft) of saprolite. It is possible that the saprolites of Coweeta formed relatively quickly at some time in the distant past and that they are "relicts" of a past weathering episode, which have persisted since that time, but this is not likely for two reasons. First, erosion on the steep slopes of Coweeta is fairly rapid, so that "relict" saprolite would probably not survive very long; therefore, saprolite would not occur at Coweeta unless it formed relatively recently, or is forming now. Secondly, clay-mineral weathering products are compatible with present-day climatic conditions (Velbel, in preparation). Either "relict" weathering profiles experience rapid mineralogical adjustments to changes in climatic conditions, or the mineral assemblages have formed under modern conditions. The former is unlikely; witness the widely documented persistence of relict weathering mineral assemblages that are clearly not related to modern climatic conditions (for example, Tarzi and Protz, 1978; Thiry and Schmitt, 1983; Guendon and Parron, 1983). Whether the 100,000-yr time-scale is an "age" for the profile or a "response time" is largely irrelevant; what is significant is that the saprolites of the southern Blue Ridge need not be relict deep weathering profiles of Tertiary age.

The "saprolitization rate" calculated in this study is 3.8 to 15.0 cm/1000 yrs, depending on which mineral must be completely transformed or destroyed before the weathered material is called saprolite; if complete transformation or destruction of all primary minerals is required, the slowest rate prevails (3.8 cm/1000 yrs). Because saprolitization is iso-volumetric, this rate does not reflect the rate of denudation or landscape

reduction (Cleaves and Costa, 1979; Costa and Cleaves, 1984); chemical weathering in the formation of saprolite only causes the weathering front to penetrate the fresh rock, leaving the volume of the landform (and the altitude of the land surface) unaffected. The actual rate of landscape reduction in deeply-weathered saprolitic landscapes is the volume rate of solid erosion (physical erosion and sediment export; for example, Büdel, 1982). If the landscape is in dynamic equilibrium and the weathering profile is steady-state (constant thickness; a highly debatable question; Berry, 1976; Cleaves and Costa, 1979; Costa and Cleaves, 1984), the landscape reduction rate equals the saprolitization rate (3.8 cm/1000 yrs). This yields a rate that is a factor of four to an order of magnitude higher than that estimated for Coweeta by Berry (1976, 1977); the disparity with Berry's rates is probably due, at least in part, to the fact that Berry did not include botanical uptake of mineral nutrients in his calculations, which means that his rates are a minimum estimate only (for example, Likens and others, 1977). The results of the calculations presented here suggest a "saprolitization rate" of about 3.8 cm/1000 yrs. If dynamic equilibrium of the landscape is assumed, then the rate of landscape lowering by (physical) erosion of the top of the weathering profile equals the saprolitization rate. The excellent accord between the modern chemical saprolitization rate and the long-term average denudation rate of 4 cm/1000 yrs for the southern Appalachians (Hack, 1980) suggests that modern chemical weathering rates are not significantly different from long-term average denudation rates, and that, in the long term, dynamic equilibrium between chemical weathering and physical denudation by erosion exists. In the short term, however, physical erosion is much more sporadic (episodic) and discontinuous. In order for dynamic equilibrium to exist in the short term, sediment export rates from watersheds should equal 600 kg/ha/yr (assuming a soil bulk density of 1.5 g/cm³). Published sediment export rates in the study area range from about 30 kg/ha/yr for undisturbed forested watersheds to around 255 kg/ha/yr for a watershed clearcut and replanted with grasses (Monk, 1975). The "normal" erosional load is therefore only about 5 to 45 percent that required to maintain dynamic equilibrium (steady state with respect to chemical weathering). Some 50 to 95 percent of the short-term physical erosion in the study area must occur as high-magnitude, low-frequency events (for example, severe storms, landslides) if long-term dynamic equilibrium is maintained. These results are consistent with the results of Grant (1983 and in press) regarding the importance of debris avalanching in the geomorphic evolution of the southern Blue Ridge. Further work on geomorphic implications of chemical weathering in the southern Appalachians is required.

KINETICS OF MINERAL WEATHERING AND COMPARISON OF NATURAL AND LABORATORY WEATHERING RATES

It is apparent from figure 3 that there is no systematic variation in any mineral weathering rate with discharge, within a given rock type. This reflects the fact that transport through the solutions is not the rate-limiting step in any weathering reaction at Coweeta. The flushing rate is

already so high, relative to the reaction rate, that increasing the flushing rate has no effect on reaction rate (Berner, 1978).

How do the rates of mineral weathering determined in this study compare with rates determined by laboratory studies? Having determined the rates from the mass balance calculations of the previous sections, it should be a relatively simple matter to convert rates in moles of mineral per hectare per yr to moles of mineral per square meter of mineral surface per sec, the dimensions commonly reported in laboratory mineral weathering studies. To do this, the amount of mineral surface area per unit area of watershed must be estimated, which can be done as follows:

A "grain size" of 1 mm was chosen as characterizing rocks and saprolites of the study area. Quantitative crystal-size distributions were not attempted, but numerous observations using hand lens, optical comparator, and binocular and petrographic microscopes indicate that the chosen value of 1 mm is the correct order of magnitude; in other words the order-of-magnitude average grain size is probably not 0.1 mm or 10 mm. Furthermore, at constant modal mineral abundance, the surface-area-normalized rate varies linearly with grain size, so that errors in the normalized rate due to errors in the grain size estimate are probably not more than one order of magnitude high or low. Grain geometry for each of the three weatherable minerals was chosen to reflect their natural habit; garnets are modeled as 1 mm-diameter spheres, plagioclase as cubes 1 mm on a side, and biotite as cylindrical discs 1 mm in diameter and 0.2 mm thick. The surface area and volume of each particle can be calculated, permitting calculation of the ratio of particle surface area to particle volume. The particle volume of a given mineral per unit volume of rock is given by modal analysis (table 2). Finally, the total volume of material affected by weathering per unit area of watershed is given by the thickness of the saprolite (20 ft, 6.1 m). Consequently, the reactive surface area of a given mineral can be estimated from the particle size and geometry and the modal petrographic analysis.

In actual application, this technique is fraught with uncertainties. The particle size estimate, while based on petrographic observations, is only an estimate of the order of magnitude of the "average" grain size and does not reflect an actual particle-size distribution. Using the modal petrographic abundances assumes that the collected thin sections accurately reflect the rock types in the basin; this is especially problematical for schists, which weather preferentially and are therefore almost certainly under-represented in the thin-section collection. Because the relative proportion of rock types (the various schists, gneisses, metasediments, et cetera, of Hatcher) are unknown, it is assumed that the thin sections do in fact accurately sample the various rock types, and the following calculations are based on simple arithmetic averages of point-count analyses. The estimated weathering rates will not, however, vary by more than one order of magnitude either way on account of errors in estimating the "average" rock composition. Modal biotite averages around 10 percent in the chosen watershed (table 2); it is highly unlikely that the actual com-

position is 1 or 100 percent biotite. As the reactive surface area is directly proportional to the modal abundance (at constant grain size), errors in weathering rates due to errors in sampling or point-counting cannot be larger than one order of magnitude either way.

Finally, of course, it is not fresh rock interacting the most with groundwater, but saprolite. The saprolite does, however, contain the same minerals as the fresh rock (although the abundances are different), and some weathering must be occurring along the rock-saprolite interface, so using "fresh" rock modal analyses is a reasonable first attempt. One further point should be noted; the lesser abundance of primary minerals in the saprolite does not necessitate a reduction in the reactive surface area. Weathering may open up internal fractures in garnet, or expand biotite, resulting in the exposure of more surface area; the etch-pitting of feldspar (Velbel, 1983) and soil garnet (Velbel, 1984b) also create larger surface areas than the original unweathered grain possessed (this phenomenon was demonstrated for olivine by Grandstaff, 1978). As a first approximation, it is assumed that the weathering-induced increase in surface area cancels the effect of decreased absolute mineral abundance brought about by mineral destruction during weathering.

Rates calculated by the above method are shown in table 3. In order to determine how closely these rates correspond to rates determined in the laboratory, it is necessary to find laboratory data that were acquired under conditions similar to the natural conditions at Coweeta. The three most important conditions are: (1) The pH of the weathering environment; mineral dissolution rates vary with pH (for example, Lasaga, 1984), so the pH's should be similar. (2) The "openness" of the system (that is, closed-system laboratory experiments are not appropriate for comparison to natural, open systems); Lin and Clemency (1981; Clemency and Lin, 1981) found experimentally that the dissolution rate of phlogopite varied by nearly three orders of magnitude depending on whether the experiment was performed in a closed or open system. Berner (1978) has also shown the dependence of dissolution rate on flushing rate. (3) The character and area of the mineral surfaces; Berner and his coworkers (Holdren and Berner, 1979; Schott, Berner, and Sjöberg, 1981), and several others (for example, Grandstaff, 1980), have shown that much of the kinetic behavior of minerals during laboratory weathering depends upon how the samples were prepared. Crushing and grinding create large quantities of fine particles, which dissolve at accelerated rates, and which would not exist in naturally fractured rock (although the results might be more directly applicable to weathering of glacial till; R. Raiswell, personal commun.). Furthermore, the surface area of the experimentally weathered mineral must be determined empirically or estimated geometrically.

One additional characteristic that useful laboratory data should possess is mutual consistency; sample pretreatment, flushing rate, and the like should be the same for all minerals of interest. This requirement makes it very difficult to use dissolution rates determined by different workers, as there is no accepted standard procedure for laboratory rate determinations.

No laboratory data sets exist that meet all the above requirements. The only published paper that comes close is that of Nickel (1973), who performed open-system dissolution experiments on a large number of crushed and size-sorted minerals (including albite, muscovite, and the only published rate data for almandine garnet), at various pH's, including 5.6. Surface areas were measured by nitrogen adsorption. All other studies were performed either at pH's significantly outside the range of Coweeta subsurface waters (5.0-6.0) or on a limited group of minerals which require "interlaboratory comparisons." Several such studies were chosen as additional bases for comparison (table 3).

Table 3 compares the rate of silica release from plagioclase and garnet calculated in this study with rates from Nickel (1973) and other workers, assuming that the laboratory rates reflect linear kinetics. The phyllosilicate weathering rates are shown as moles of mica weathered, rather than moles of silica released, because the weathering reaction of biotite at Coweeta is a solid-solid transformation in which silica is not released.

TABLE 3
Comparison of natural and laboratory weathering rates

Silica release rates (moles/m ² /sec)				
	pH	System		
Albite	5.6	Open	3.12×10^{-12}	Nickel, 1973
	4.5 - 5.1	Closed	4.41×10^{-12}	Busenberg and Clemency, 1976
		Closed	1.26×10^{-11}	Holdren and Berner, 1979
	5.1	Open	1.51×10^{-11}	Chou and Wollast, 1985
	5	Closed	2.16×10^{-11}	Holdren and Speyer, 1985
Oligoclase			8.9×10^{-12}	This study
Almandine			1.1×10^{-11}	Nickel, 1973
			3.8×10^{-12}	This study
"Total" weathering rate (moles mineral/m ² /sec)				
Phlogopite*			2.0×10^{-10}	Clemency and Lin, 1981
Biotite			1.2×10^{-13}	This study

* pH 3 to 4.6

Given that mineral compositions are probably not identical in any of the tabulated cases, and that mineral surface areas for the natural system at Coweeta are only estimates which may be subject to errors of several orders of magnitude, the fact that natural and laboratory rates for plagioclase and garnet weathering compare so favorably (within about one order of magnitude) is remarkable; in fact the results of field and laboratory weathering rate determinations are probably identical within the limits of error. The higher laboratory rates could be due to any of a number of factors. Adhering fine particles created by crushing during sample preparation would render artificial mineral surfaces more reactive than their natural counterparts, a phenomenon demonstrated and discussed by Holdren and Berner (1979) and Schott, Berner, and Sjöberg (1981); neither Nickel (1973) nor most other workers summarized in table 3 employed any pretreatment to remove such artificial fines. Furthermore, if sample preparation generated similar quantities of fines for both minerals, both laboratory rates should be increased by approximately the

same proportion, so that the *ratio* of the reaction rates in nature (surfaces without fines) is similar to that in the laboratory (with fines). The ratio of garnet weathering rate to plagioclase is around 4.2 in nature, as compared to 3.6 in the laboratory. Almandine garnet apparently weathers about four times faster than plagioclase under similar conditions. Alternatively, sample preparation may affect the density and/or distribution of defects, which would in turn affect dissolution rates (for example, Holdren and Speyer, 1985).

A third possible source of the discrepancy between natural and laboratory estimates of weathering rates is error in estimating reactive surface area in the natural system. As noted above, active reactive mineral surface areas in the saprolites of Coweeta could be greater or less than the values estimated using modal abundance and geometry. If the mean grain size is actually less than 1 mm, or if fracturing or etch-pitting expose additional surface area not taken into account in estimating the bulk surface area from grain geometry, then the actual surface area could be greater than that estimated above; this would magnify the discrepancy between laboratory rates and the estimates of this study by increasing the surface area thereby reducing the surface-area-normalized rate. Alternatively, weathering in the saprolite may have depleted the absolute modal abundance of primary minerals to amounts significantly lower than the amounts estimated from modal analysis of bedrock samples; this would reduce the actual surface area relative to the estimated value and bring the surface-area-normalized rates into closer agreement with the laboratory rates. In nature, the aforementioned factors compete with one another, with grain size diminution, exposure of fractures, and etch-pitting acting to increase surface area while destruction of primary minerals acts to decrease the absolute abundance of mineral material available to contribute to the surface area. In this study, these competing effects are assumed to cancel one another out, but it is clear that this is only an approximation.

The much greater disparity between the rate numbers for micas could have any of several causes: (1) Phlogopite is the iron-free end-member of biotite, yet the oxidation of iron during weathering has profound effects on biotite weathering (for example, Velbel, 1984a, for a review of this subject); therefore, comparing phlogopite with biotite is probably not representative. (2) Clemency and Lin's (1981) experiments were performed at pH 3 to 4.7, one to three units lower than natural waters at Coweeta; this could account for orders of magnitude difference in rates. (3) The "rate" calculated for biotite weathering at Coweeta is for the transformation of biotite layers to vermiculite layers; Clemency and Lin's (1981) rate is for dissolution of phlogopite (that is, breakdown of the tetrahedral lattice). The reactions are radically different, again rendering direct comparison of rates inappropriate.

To the extent that reaction mechanisms are similar in laboratory and natural settings (in this study, plagioclase and garnet meet this criterion), it appears that laboratory rates mimic natural rates to within about

an order of magnitude, even in the absence of specifically-determined flow rates.

Recently, Pačes (1983) performed a similar mass-balance calculation for sodium only and used it to calculate the rate of plagioclase weathering in his study area. He found that natural rates average about one to three orders of magnitude lower than laboratory rates and attributed the difference to (1) the difference between natural and artificial mineral surfaces and (2) difficulties in estimating the reactive surface area of minerals in the natural environment, both factors discussed above. Still more recently, Siegel (1984) calculated approximately equal (bulk) rates of olivine and plagioclase feldspar weathering in a mafic watershed of northeastern Minnesota, despite the fact that the feldspar:olivine ratio in the watershed is about 25:1. Siegel noted, however, that the implied 25-fold preferential destruction of olivine relative to feldspar compares favorably with laboratory kinetic data for the same minerals (Siegel and Pfannkuch, 1984).

Mutual consistency between mass balance studies is also evident as table 4 shows. Table 4 shows rates of plagioclase feldspar weathering calculated in four different published geochemical mass balance studies of eleven different watersheds. Despite differences in computational methods, parent lithology, and climate, rates of plagioclase weathering in small watersheds calculated by geochemical mass balance models agree within a factor of five. Normalizing the watershed-averaged rate to the modal abundance of plagioclase (to allow for the possibility that the variations merely reflect the different abundance of plagioclase per unit watershed area in the different cases) does not narrow the range substantially (table 4), but the grain size and reactive surface area (among other factors) are probably much more important than modal abundance in determining how much plagioclase is able to interact with percolating solutions,

TABLE 4
Plagioclase weathering rates from watershed mass balance studies

Watershed		Rate (moles/ha/yr)	Modal % feldspar	Normalized rate (moles/ha/yr/% feldspar)
Coweeta	2	This study 613		
	18	453		
	34	497		
	36	732		
	14	274		
	27	305	8.3	36.7
	32	308		
Pond Branch		Cleaves and others, 1970 148	10.6	14.0
Trnavka	X-O	Paces, 1983 210	(19)	11.1
	X-9	550	14	39.3
Filson Creek		Siegel, 1984 235		
Ratio $\frac{\text{Rate}_{\max}}{\text{Rate}_{\min}} = 4.95$		Ratio $\frac{\text{Normalized rate}_{\max}}{\text{Normalized rate}_{\min}} = 3.54$		

so the scatter of table 4 is not surprising. The major source of uncertainty in any normalization of field rate data is the reactive surface area of the mineral in the weathering profile, as noted above.

Given the potential uncertainties, the general accord of the results of these independent mass-balance studies with each other and with laboratory studies lend credence to the idea that mass-balance studies are a reliable method of estimating mineral weathering rates in nature (Clayton, 1979).

CLAY MINERAL FORMATION AND RATES OF HYDROGEN ION CONSUMPTION

The mutual consistency of calculated mineral weathering rates with results of short- and long-term geomorphic studies, other mass-balance studies, and laboratory kinetic studies suggests that rates of important geological and geochemical processes are accurately quantified by the mass balance method. In addition to demonstrating that different lines of investigation indicate comparable rates, however, one further objective of geochemical modeling is to make potentially useful (and testable) predictions about natural phenomena. Two areas in which useful quantitative predictions might be made on the basis of geochemical mass balance models like the above are: (1) calculation of rates of biomass accumulation within a watershed from mass balance budgets, and (2) determining the rate at which inorganic transformations in the weathering profile consume hydrogen ion, thereby contributing to the amelioration of acid precipitation effects. This study's calculated botanical uptake rates are only now being evaluated, so no conclusions can be safely drawn at present regarding the possible ecological significance of the model results. Net consumption of hydrogen ion by the sum of the mineral transformations can, however, be evaluated and compared with atmospheric loading on these watersheds.

The overall weathering reactions taking place within the weathering profiles of Coweeta are summarized in eqs 1 to 5 above; rates for the first three have been calculated and discussed above, and the consumption of hydrogen ion by these three primary-mineral weathering reactions is easily determined. However, hydrogen ion is also involved in the neoformation reactions of gibbsite and kaolinite (eqs 4 and 5), so estimating net acid consumption requires that clay mineral formation rates be estimated as well.

Rates of kaolinite and gibbsite neoformation are estimated as follows: three control watersheds for which dissolved silica efflux data are available are used. The amount of silica released by the weathering of primary minerals is calculated from the results of the mass balance calculations (shown in fig. 4) and the stoichiometries of reactions 1, 2, and 3. Botanical uptake of silica, like that of sodium, is assumed to be negligible. The net efflux of silica from the watersheds (stream efflux minus precipitation input, from Swank and Douglass, 1977) is then subtracted from this estimated amount of silica released by primary-mineral weathering, giving the amount of silica retained in the weathering profiles which is not accounted for in reactions 1, 2, and 3—in other words, the silica

retained by kaolinite formation, reaction 5. This determines the kaolinite formation rate.

Similar methods are used to determine the amount of aluminum released by the primary mineral weathering reactions. Because no data exist on dissolved aluminum fluxes through Coweeta watersheds, two sets of assumptions are made, resulting in two different scenarios for the behavior of aluminum. One scenario assumes no atmospheric input of aluminum, no botanical cycling of Al, *and* no dissolved export. In this scenario, all aluminum released by primary-mineral weathering that is *not* consumed by formation of kaolinite is assumed to be retained within the weathering profile as gibbsite. In the second scenario, organic chelation (for example, Graustein, 1981) drives Al solubility to such high levels that all Al not combined with silica to form kaolinite is exported from the watersheds *via* streams. Because gibbsite is almost ubiquitous in Coweeta watersheds, this scenario is not realistic, but it represents the most extreme allowable degree of Al mobility, so it is included for completeness.

The mass balances constructed for each watershed using the method discussed above permit estimation of kaolinite and gibbsite formation rates and their contribution to the hydrogen ion budget using the stoichiometries of reactions 4 and 5 above. Results of the calculations for three Coweeta control watersheds are shown in table 5.

TABLE 5
Net inorganic hydrogen ion consumption (moles/ha/yr)

Scenario/Watershed	2	18	27
1. Al retention	367	700	283
2. Total Al release	558	1340	752

Data for the pH of rain in watersheds 2 and 27 are not available. However, the data of Swank and Douglass (1977) for watershed 18 indicate that, for the period 1972 to 1976, average annual rainfall was 223 cm, with a weighted mean hydrogen ion content corresponding to a pH of 4.44, giving an atmospheric hydrogen ion influx of around 810 moles/ha/yr. It can be seen from table 5 that mineral weathering reactions in watershed 18 are occurring rapidly enough to consume at least 70 percent of the atmospherically deposited acidity. Given that comparable silicate mineral weathering rates seem to obtain in other Coweeta watersheds and other geologic and geographic regions as well (table 4), the role of silicate bedrock weathering in ameliorating the effects of acid precipitation may be considerably greater than is presently believed. Unfortunately, data do not presently exist that would permit evaluation of non-atmospheric acid sources in the overall hydrogen ion budget.

CONCLUSIONS

Weathering of metamorphic rocks in the U.S. Forest Service Coweeta Hydrologic Laboratory of the southern Blue Ridge has produced a deeply-weathered residuum (saprolite) with an average thickness of 6.1 m (20 ft) capped with about 30.5 cm (1 ft) of soil. The transformation of rock to

saprolite is due to the weathering of three minerals, biotite mica, almandine garnet, and sodic plagioclase feldspar. Other major rock-forming minerals, including quartz, muscovite, kyanite, sillimanite, and staurolite, are not detectably weathered.

Published data on the elemental composition of forest biomass in the study watersheds, elemental fluxes via rain and streams in the study watersheds, and stoichiometries of (petrographically determined) mineralogic transformations can be combined to construct and constrain a geochemical mass balance for an individual forested watershed. Rates of weathering for each of the three major weatherable minerals can then be calculated, as can the rates of mineral nutrient uptake by the forest biota. These calculations yield several interesting results: (1) The time required to deplete completely 6.1 m (20 ft) of rock of its biotite, garnet, and plagioclase is around 1.6×10^5 yrs under present conditions, suggesting a time scale of around 10^5 yrs for the formation of 6.1 m (20 ft) of saprolite. The "weathering front" penetrates the rock at a rate of around 3.8 cm (0.125 ft) per thousand yrs. If the rate of physical removal of weathered regolith is equal to this rate (that is, if the saprolite thickness is steady-state) the denudation rate determined here is in excellent accord with the "average" denudation rate for the Appalachians. (2) Relationships between concentration and discharge (flushing rate) and the results of the mass-balance calculations confirm that there is no flushing-rate dependence (stirring dependence of Berner, 1978) in the natural weathering system at Coweeta. (3) When normalized to the estimated mineral surface area in the watersheds, rates of garnet and plagioclase weathering are no more than approximately one to two orders of magnitude slower than rates determined in laboratory experiments under similar hydrogeochemical conditions. Two possible sources of this discrepancy are (A) the character of artificially-treated mineral surfaces, which renders them more reactive than their natural counterparts, and/or (B) difficulties in estimating reactive mineral surface area in natural systems.

The results of geochemical mass-balance calculations are quantitatively consistent with laboratory studies of mineral weathering and geomorphological studies of regional denudation rates. The relatively good accord between field and laboratory geochemical and geomorphologic results suggests that refinement of laboratory kinetic data and field surface area determinations should rank high among future research priorities. Future work linking natural and laboratory observations of geochemical and ecological processes and products by way of integrated, theoretically-based mass-balance models may produce unified biogeochemical models of considerable explanatory and predictive value for problems of acid precipitation effects, forest regeneration rates, land and ecosystem management, and the geochemical and geomorphic history of the Earth's surface.

ACKNOWLEDGMENTS

This paper is based largely on portions of the author's Ph.D. dissertation at Yale University. I am most grateful to Professor Robert A. Berner for his guidance and support. I also thank E. T. Cleaves, B. L. Sawhney,

K. K. Turekian, R. J. Tracy, W. T. Swank, R. Beale, J. E. Douglass, D. Nahon, J. L. Berry, R. D. Hatcher, Jr., M. C. Monaghan, J. Rodgers, D. Hurd, A. C. Lasaga, R. Newton, R. April, E. L. Sjöberg, M. Pavich, B. F. Jones, G. Sposito, J. R. Kramer, R. Wollast, M. Meybeck, W. Murphy, H. W. Nesbitt, and, especially, J. Dowd, W. C. Graustein, B. P. Boudreau, and D. Brandt Velbel, for their comments, criticisms, and encouragement. Reviews by O. P. Bricker and J. I. Drever contributed greatly to the preparation of the final manuscript and are gratefully acknowledged. This research was supported by National Science Foundation grant EAR 80-07815 to R. A. Berner and was performed under a cooperative agreement with the U.S.D.A. Forest Service, Southeast Forest Experiment Station.

REFERENCES

- Becker, G. F., 1895, A reconnaissance of the goldfields of the southern Appalachians: U.S. Geol. Survey, 16th Ann. Rept., pt. 3, p. 251-331.
- Berner, R. A., 1971, *Principles of Chemical Sedimentology*: New York, McGraw-Hill, 240 p.
- , 1978, Rate control of mineral dissolution under earth surface conditions: *Am. Jour. Sci.*, v. 278, p. 1235-1252.
- , 1981, Kinetics of Weathering and Diagenesis, in Lasaga, A. C., and Kirkpatrick, R. J., eds., *Kinetics of Geochemical Processes*: Mineralog. Soc. America Rev. in Mineralogy, v. 8, p. 111-134.
- Berry, J. L., 1977, Chemical weathering and geomorphological processes at Coweeta, North Carolina: *Geol. Soc. America Abs. with Programs*, v. 9, p. 120.
- Boring, L. R., Monk, C. D., and Swank, W. T., 1981, Early regeneration of a clear-cut southern Appalachian forest: *Ecology*, v. 62, p. 1244-1253.
- Bricker, O. P., Godfrey, A. E., and Cleaves, E. T., 1968, Mineral-water interaction during the chemical weathering of silicates, in *Trace Inorganics in Water*: Am. Chem. Soc. Adv. in Chemistry Ser., v. 73, p. 128-142.
- Büdel, J., 1982, *Climatic Geomorphology* (translated by Fischer, L. and Busche, D.): Princeton, N.J., Princeton Univ. Press, 433 p.
- Busenberg, E., and Clemency, C. V., 1976, The dissolution kinetics of feldspars at 25°C and 1 atm CO₂ partial pressure: *Geochim. et Cosmochim. Acta*, v. 40, p. 41-49.
- Chou, L., and Wollast, R., 1984, Study of the weathering of albite at room temperature and pressure with a fluidized bed reactor: *Geochim. et Cosmochim. Acta*, v. 48, p. 2205-2217.
- Claassen, H. C., and White, A. F., 1979, Application of geochemical kinetic data to groundwater systems, in Jenne, E. A., ed., *Chemical modeling in aqueous systems*: Am. Chem. Soc. Symposium Ser., no. 93, p. 771-793.
- Clayton, J. L., 1979, Nutrient supply to soil by rock weathering, in *Impact of intensive harvesting on forest nutrient cycling*: Syracuse, N.Y., State Univ. of New York, College of Environmental Sci. and Forestry, p. 75-96.
- Cleaves, E. T., and Costa, J. E., 1979, Equilibrium, Cyclicality, and Problems of Scale-Maryland's Piedmont Landscape: *Maryland Geol. Survey, Inf. Circ.*, v. 29, 32 p.
- Cleaves, E. T., Fisher, D. W., and Bricker, O. P., 1974, Chemical weathering of serpentinite in the eastern Piedmont of Maryland: *Geol. Soc. America Bull.*, v. 85, p. 437-444.
- Cleaves, E. T., Godfrey, A. E., and Bricker, O. P., 1970, Geochemical balance of a small watershed and its geomorphic implications: *Geol. Soc. America Bull.*, v. 81, p. 3015-3032.
- Clemency, C. V., and Lin, F. C., 1981, Dissolution kinetics of phlogopite. II. Open system using an ion-exchange resin: *Clays and Clay Minerals*, v. 29, p. 107-112.
- Costa, J. E., and Cleaves, E. T., 1984, The Piedmont landscape of Maryland: a new look at an old problem: *Earth Surface Processes and Landforms*, v. 9, p. 59-74.
- Day, F. P., and Monk, C. D., 1977, Seasonal nutrient dynamics in the vegetation on a southern Appalachian watershed: *Am. Jour. Botany*, v. 64, p. 1126-1139.
- Douglass, J. E., and Swank, W. T., 1975, Effects of management practices on water quality and quantity: Coweeta Hydrologic Laboratory, North Carolina: U.S. Dept. Agr. Forest Service Gen. Tech. Rept. NE-13, p. 1-13.

- Drever, J. I., 1971, Chemical weathering in a subtropical igneous terrain, Rio Ameca, Mexico: *Jour. Sed. Pet.*, v. 41, p. 951-961.
- 1982, *The Geochemistry of Natural Waters*: Englewood Cliffs, N.J., Prentice-Hall, Inc., 388 p.
- Feth, J. H., Roberson, C. E., and Polzer, W. L., 1964, Sources of mineral constituents in water from granitic rocks, Sierra Nevada: U.S. Geol. Survey Water-Supply Paper 1535-I, 70 p.
- Fritz, B., 1975, Étude thermodynamique et simulation des réactions entre minéraux et solutions application à la géochimie des altérations et des eaux continentales: Univ. Louis Pasteur de Strasbourg, *Sci. Géol.*, Mem. 41, 152 p.
- Garrels, R. M., 1967, Genesis of some groundwaters from igneous rocks, in Abelson, P. H., ed., *Researches in Geochemistry*, v. 2: New York, Wiley, p. 405-420.
- Garrels, R. M., and Mackenzie, F. T., 1967, Origin of the chemical compositions of some springs and lakes, in Stumm, W., ed., *Equilibrium concepts in natural water systems*: Am. Chem. Soc. Adv. in Chemistry Ser., v. 67, p. 222-242.
- Grandstaff, D. E., 1978, Changes in surface area and morphology and the mechanism of forsterite dissolution: *Geochim. et Cosmochim. Acta*, v. 42, p. 1899-1901.
- 1980, The dissolution rate of forsteritic olivine from Hawaiian beach sand, in *Proceedings of the 3rd International symposium on water-rock interaction*: Edmonton, Canada, p. 72-74.
- Grant, W. H., 1983, Debris avalanching and slow alluviation, a mechanism for rapid valley growth: *Geol. Soc. America Abs. with Programs*, v. 15, p. 55.
- Graustein, W. C., 1976, Organic complexes and the mobility of iron and aluminum in soil profiles: *Geol. Soc. America Abs. with Programs*, v. 6, p. 891.
- Graustein, W. C., ms, 1981, The effects of forest vegetation on solute acquisition and chemical weathering: A study of the Tesuque watersheds near Santa Fe, New Mexico: Ph.D. dissert., Yale Univ., 645 p.
- Guendon, J. L., and Parron, C., 1983, Bauxites et ocre Crétacées du sud-est de la France: Mécanismes de l'altération de roches sédimentaires: *Internat. Colloquium CNRS on the Petrology of Weathering and Soils, Field Trip Guidebook*, 142 p.
- Hack, J. T., 1980, Rock control and tectonism — their importance in shaping the Appalachian highlands: U.S. Geol. Survey Prof. Paper 1126-B, 17 p.
- Hatcher, R. D., Jr., 1971, The geology of Rabun and Habersham Counties, Georgia: *Georgia Geol. Survey Bull.* 83, 48 p.
- 1974, An Introduction to the Blue Ridge Tectonic History of Northeast Georgia: *Georgia Geol. Survey Guidebook* 13-A, 60 p.
- 1976, Introduction to the Geology of the Eastern Blue Ridge of the Carolinas and nearby Georgia: *Carolina Geol. Soc. Field Trip Guidebook*, 53 p.
- 1978, Tectonics of the western Piedmont and Blue Ridge, Southern Appalachians, review and speculation: *Am. Jour. Sci.*, v. 278, p. 276-304.
- 1979, The Coweeta Group and Coweeta Syncline: Major features of the North Carolina-Georgia Blue Ridge: *Southeastern Geology*, v. 21, p. 17-29.
- 1980, *Geologic Map and Mineral Resources Summary of the Prentiss Quadrangle, North Carolina, including Geologic Map of the Coweeta Laboratory*: North Carolina Dept. Nat. Resources and Community Devel., Geol. Survey Sec., GM 167-SW and MRS 167-SW.
- Hatcher, R. D., Jr., and Butler, J. R. (compilers), 1979, *Guidebook for southern Appalachian Field Trip in the Carolinas, Tennessee, and northeastern Georgia*: *Internat. Geol. Correlation Program, North Carolina Geol. Survey*, 117 p.
- Helgeson, H. C., Garrels, R. M., and Mackenzie, F. T., 1969, Evaluation of irreversible reactions in geochemical processes involving minerals and aqueous solutions — II. Application: *Geochim. et Cosmochim. Acta*, v. 33, p. 455-481.
- Hewlett, J. D., 1961, Soil moisture as a source of base flow from steep mountain watersheds: U.S. Dept. Agr. Forest Service, Southeastern Forest Expt. Sta., Sta. Paper 132, 11 p.
- Hewlett, J. D., and Douglass, J. E., 1968, Blending forest uses: U.S. Dept. Agr. Forest Service Research Paper SE-37, 15 p.
- Hewlett, J. D., and Hibbert, A. R., 1963, Moisture and energy conditions within a sloping soil mass during drainage: *Jour. Geophys. Research*, v. 68, p. 1081-1087.
- 1966, Factors affecting the response of small watersheds to precipitation in humid areas, in *International Symposium on Forest Hydrology, Proceedings of a National Science Foundation Advanced Science Seminar*: New York, Pergamon Press, p. 275-290.

- Holdren, G. R., Jr., and Berner, R. A., 1979, Mechanism of feldspar weathering — I. Experimental studies: *Geochim. et Cosmochim. Acta*, v. 43, p. 1161-1171.
- Holdren, G. R., Jr., and Speyer, P. M., 1985, Reaction rate-surface area relationships during the early stages of weathering — I. Initial observations: *Geochim. et Cosmochim. Acta*, v. 49, p. 675-681.
- Horton, J. H., and Hawkins, R. H., 1964, The importance of capillary pores in rain-water percolation to the ground water table: E. I. du Pont de Nemours and Co., Savannah River Plant, DPSPU 64-30-23, 13 p.
- Hudson, C., 1976, *The Southeastern Indians*: Knoxville, The Univ. of Tennessee Press, 573 p.
- Johnson, P. L., and Swank, W. T., 1973, Studies of cation budgets in the southern Appalachians on four experimental watersheds with contrasting vegetation: *Ecology*, v. 54, p. 70-80.
- Keel, B. C., 1976, *Cherokee Archaeology*: Knoxville, The Univ. of Tennessee Press, 290 p.
- Lasaga, A. C., 1981a, Rate Laws of Chemical Reactions, in Lasaga, A. C., and Kirkpatrick, R. J., eds., *Kinetics of Geochemical Processes*: Mineralog. Soc. America Rev. in Mineralogy, v. 8, p. 1-68.
- 1981b, Transition State Theory, in Lasaga, A. C., and Kirkpatrick, R. J., eds., *Kinetics of Geochemical Processes*: Mineralog. Soc. America Rev. in Mineralogy, v. 8, p. 135-164.
- 1981c, The Atomistic Basis of Kinetics: Defects in Minerals, in Lasaga, A. C., and Kirkpatrick, R. J., eds., *Kinetics of Geochemical Processes*: Mineralog. Soc. America Rev. in Mineralogy, v. 8, p. 261-319.
- 1984, Chemical kinetics of water-rock interactions: *Jour. Geophys. Research*, v. 89, p. 4009-4025.
- Likens, G. E., Bormann, F. H., Pierce, R. S., Eaton, J. S., and Johnson, N. M., 1977, *Biogeochemistry of a Forested Ecosystem*: New York, Springer-Verlag, 146 p.
- Lin, F. C., and Clemency, C. V., 1981, Dissolution kinetics of phlogopite. I. Closed system: *Clays and Clay Minerals*, v. 29, p. 101-106.
- Lindsay, W. L., 1979, *Chemical Equilibria in Soils*: New York, John Wiley and Sons, 449 p.
- Marchand, D. E., 1971, Rates and modes of denudation, White Mountains, Eastern California: *Am. Jour. Sci.*, v. 270, p. 109-135.
- 1974, Chemical weathering, soil development, and geochemical fractionation in a part of the White Mountains, Mono and Inyo Counties, California: *U.S. Geol. Survey Prof. Paper* 352-J, p. 379-424.
- Miller, W. R., and Drever, J. I., 1977, Chemical weathering and related controls on surface water chemistry in the Absaroka Mountains, Wyoming: *Geochim. et Cosmochim. Acta*, v. 41, p. 1693-1702.
- Monk, C. D., 1975, Nutrient losses in particulate form as weir pond sediments from four unit watersheds in the southern Appalachians, in Howell, F. G., Gentry, J. B., and Smith, M. H., eds., *Mineral Cycling in Southeastern Ecosystems*: ERDA Symposium Series (CONF-740513), p. 862-867.
- Monk, C. D., Crossley, D. A., Jr., Todd, R. L., Swank, W. T., Waide, J. B., and Webster, J. R., 1977, An overview of nutrient cycling research at Coweeta Hydrologic Laboratory, in Correll, D. L., ed., *Watershed Research in Eastern North America*: Washington, D.C., Smithsonian Inst., p. 35-50.
- Mooney, J., 1900, Myths of the Cherokee: *Bur. American Ethnology* 19th Ann. Rept., 1897-1898, Part I.
- Nickel, E., 1973, Experimental dissolution of light and heavy minerals in comparison with weathering and intracrystalline dissolution: *Contr. Sedimentology*, v. 1, p. 1-68.
- Pačes, T., 1973, Steady-state kinetics and equilibrium between ground water and granitic rock: *Geochim. et Cosmochim. Acta*, v. 37, p. 2641-2663.
- 1976, Kinetics of natural water systems, in *Interpretation of Environmental Isotope and Hydrochemical Data in Groundwater Hydrology*: Vienna, Internat. Atomic Energy Agency, p. 85-108.
- 1978, Reversible control of aqueous aluminum and silica during the irreversible evolution of natural waters: *Geochim. et Cosmochim. Acta*, v. 42, p. 1487-1493.
- 1983, Rate constants of dissolution derived from the measurements of mass balance in hydrological catchments: *Geochim. et Cosmochim. Acta*, v. 47, p. 1855-1863.

- Plummer, L. N., and Back, W., 1980, The mass balance approach: application to interpreting the chemical evolution of hydrologic systems: *Am. Jour. Sci.*, v. 280, p. 130-142.
- Schott, J., Berner, R. A., and Sjöberg, E. L., 1981, Mechanism of pyroxene and amphibole weathering—I. Experimental studies of iron-free minerals: *Geochim. et Cosmochim. Acta*, v. 45, p. 2123-2135.
- Siegel, D. I., 1984, The effect of kinetics on the geochemical balance of a small watershed on mafic terrain: EOS, *Am. Geophys. Union Trans.*, v. 65, p. 211.
- Siegel, D. I., and Pfannkuch, H. O., 1984, Silicate mineral dissolution at pH 4 and near standard temperature and pressure: *Geochim. et Cosmochim. Acta*, v. 48, p. 197-201.
- Sklash, M. G., and Farvolden, R. N., 1982, The use of environmental isotopes in the study of high-runoff episodes in streams, in Perry, E. C., Jr., and Montgomery, C. W., eds., *Isotope Studies of Hydrologic Processes*: DeKalb, Northern Illinois Univ. Press, p. 65-73.
- Swank, W. T., and Douglass, J. E., 1975, Nutrient Flux in Undisturbed and Manipulated Forest Ecosystems in the Southern Appalachian Mountains: *Assoc. Internat. des Sci. Hydrol. Symposium*, Tokyo, Decembre 1975, Pub. 117, p. 445-456.
- 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*: Washington, D.C., Smithsonian Inst., p. 343-364.
- Tarzi, J. G., and Protz, R., 1978, The occurrence of lepidocrocite in two well-drained Ontario soils: *Clays and Clay Mineral*, v. 26, p. 448-451.
- Thiry, M., and Schmitt, J. M., 1983, Silicifications and Paleosilcretes in the Tertiary detrital series of the Paris Basin: *Internat. Colloquium CNRS on the Petrology of Weathering and Soils, Field Trip Guidebook*, 33 p.
- Velbel, M. A., 1982, Weathering and saprolitization in the southern Blue Ridge: *Internat. Cong. on Sedimentology*, 11th, Abs., p. 171-172.
- 1983, A dissolution-reprecipitation mechanism for the pseudomorphous replacement of plagioclase feldspar by clay minerals during weathering, in Nahon, D., and Noack, Y., eds., *Pétrologie des Altérations et des Sols*, v. I: *Mem. Sci. Géol.*, v. 71, p. 139-147.
- 1984a, Weathering processes of rock-forming minerals, in Fleet, M. E., ed., *Environmental Geochemistry: Mineralog. Assoc. Canada Short Course Notes*, v. 10, p. 67-111.
- 1984b, Natural weathering mechanisms of almandine garnet: *Geology*, v. 12, p. 631-634.
- 1985, Hydrogeochemical Constraints on Mass Balances in Forested Watersheds of the Southern Appalachians, in Drever, J. I., ed., *The Chemistry of Weathering*: Holland, D. Reidel, p. 231-247.
- White, A. F., and Claassen, H. C., 1980, A case for diffusion kinetics as a control on the weathering of glassy volcanic rocks at 25°C: *Internat. Symposium on Water-Rock Interaction*, 3d, Edmonton, Canada, Proc., p. 163-165.
- White, A. F., Claassen, H. C., and Benson, L. V., 1980, The effect of dissolution of volcanic glass on the water chemistry in a tuffaceous aquifer, Rainier Mesa, NV: *U.S. Geol. Survey Water-Supply Paper* 1535-Q, 34 p.
- Winner, M. D., Jr., 1977, Ground-water resources along the Blue Ridge Parkway, N.C.: *U.S. Geol. Survey Water Resources Inv.* 77-65, 166 p.