NUTRIENT SUPPLY TO SOIL BY ROCK WEATHERING

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Abstract.—Rates of nutrient release by rock weathering can be estimated by a variety of direct and indirect techniques. Direct techniques include laboratory studies of mineral weathering and field studies of mineral grain depletion in soils of known age. The relationship between weathering rind thickness and age also provides a measure of rock weathering rate. Indirect techniques include watershed and lysimeter studies of chemical transfer rates. These studies require solution of a mass balance equation to account for all gains and losses of nutrients. Therefore, it is essential to have reliable estimates of precipitation chemistry, biomass nutrient accrual, nutrient gains to the soil, and losses from the system measured in a stream or with a lysimeter. Mass balance techniques provide useful estimates of nutrient gains for all elements except phosphorus, which is too immobile to estimate by this technique. Elemental release from rock weathering is highly variable, and strongly dependent on the primary mineralogy of rock.

Additional key words: Forest soil nutrition, nutrient budgets, geochemical cycling, rock-weathering rates.

INTRODUCTION

Of the 16 elements known to be essential to growth of higher plants, and the few thought to be beneficial, most are supplied through the weathering of bedrock. The macronutrients supplied by rock weathering include: phosphorus, potassium, calcium, and magnesium. Much of the sulfur supply also comes from rock weathering. Iron and the micronutrients molybdenum, boron, copper, manganese, and zinc are provided from rock. Silicon, sodium, and selenium, elements known to be beneficial to some plants, are primarily provided by weathering of rock. The macronutrients are some of the most abundant elements in the earth's crust and in most igneous rocks; for example, calcium ranks fifth, potassium seventh, magnesium eighth, and sulfur fourteenth in abundance (Mason 1966). Micronutrient elements are sufficiently abundant in bedrock to provide an adequate supply to most plants. Data on rates of release of micronutrients are scarce, however, and replenishment supply rates are not available. The only micronutrient discussed in this paper is iron.

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Rocks vary greatly in their mineralogy and chemistry, and hence, capacity to supply nutrient elements to soil. Sedimentary rocks often are deficient in one or more nutrient elements because the processes leading to formation of sedimentary rocks tend to disperse some minerals and concentrate others. Sandstones often are siliceous and low in bases because of concentration of quartz; limestones are poor in aluminosilicate minerals and form few clay minerals. In contrast, processes of igneous and metamorphic rock formation tend to combine and homogenize mineral-forming elements. In most cases, igneous and metamorphic rocks have the potential of supplying adequate nutrients to the soil-plant system.

The question then arises, at what rates are these elements supplied to the soil, and in what forms? We become particularly concerned with rates of nutrient supply as our ability and desire to intensively manage and harvest timber increases and our technology progresses toward more complete utilization of the wood resource. Intensive harvesting and more complete utilization both lead to increased nutrient removal from forest lands. We are also concerned with the forms of nutrient supply from rock weathering as they affect availability for plant growth.

In this paper, I present techniques used by researchers in a variety of fields to estimate rates of rock weathering. Some of these estimates were designed to provide data on nutrient accrual to ecosystems, but the majority are not primarily nutrient studies. I evaluate the suitability of these techniques for predicting nutrient gains and present rates of rock weathering from a variety of climates and parent materials.

ROCK WEATHERING AND PEDOGENESIS

Weathering processes are a continuous readjustment toward a chemical equilibrium the rock makes in response to the differing environmental conditions at the earth's surface. The primary mineralogy of a rock reflects the temperature, pressure, and chemical composition during its formation, often at great depth or at high temperature in the case of metamorphic and igneous rocks. At the surface, lower temperatures and pressures, the presence of water, various organic and inorganic acids, and many other compounds dictate a state of disequilibrium. The secondary weathering products are formed as the rock adjusts to the surface environment.

The zone of rock weathering extends from the earth's surface to depths ranging from less than a meter to several hundred meters, depending upon climate, lithology, age, and prior weathering history.

Initial weathering must precede soil formation in hard rocks, but accompanies it in soft, weakly consolidated rock. The weathering of primary minerals within the solum, termed pedochemical weathering by Jackson and Sherman (1953), is a primary concern of this paper. Because nutrient release takes place within the rooting zone, studies of pedochemical weathering are useful for determining gains of nutrients to soil. Processes and products of pedochemical weathering are well documented in the literature, but there is a notable lack of published research on rates of pedochemical weathering.

The intensity of chemical weathering in the soil profile is generally greater than in underlying rock or in rock exposed at the surface. Because of the wetter environment near the surface, greater leaching affects this zone, and the organic compounds in the soil aid in the weathering process.

There are many general references on processes and products of chemical weathering (see Loughnan 1969, Ollier 1969, Carroll 1970). Studies of rates of chemical weathering are much less common in the literature. We can commonly find data on relative rates of weathering of individual minerals, sometimes even tied to climate and geographic location, but the absolute rates necessary for computing nutrient release are difficult to obtain.

Minerals weather at different rates depending upon their chemical composition and crystal structure. Knowledge of these rate differences and an understanding of their causes is useful if we are to relate data on rock weathering and water and soil chemistry to nutrient gains in forest ecosystems.

For silicate minerals, the amount of silicate-tetrahedron linkage and amount of base elements per unit cell of the crystal structure affect susceptibility and hence rate of weathering. As tetrahedral bonding increases and as degree of basicity decreases, minerals are increasingly resistant to weathering. Goldich (1938) arranged the common rock-forming minerals into two stability series, one for ferromagnesian minerals and one for feldspars and quartz. Keller (1954) was able to provide bonding energies for these minerals that substantiated Goldich's stability series. In simplified form, ferromagnesian mineral stability is as follows: olivine < pyroxenes < amphiboles < biotite. For nonferromagnesian minerals: Ca-plagioclase < Na-plagioclase < K-feldspars < muscovite < quartz. To roughly compare the two series, olivine is about as stable as An_{65-80} plagioclase (bytownite), and biotite is about as stable as the sodic end-member of the plagioclase series, albite.

The stability series concept is very useful in explaining differential weathering rates of minerals within a single rock type, or for comparing weathering rates of two different rock types containing grossly different mineralogies. We expect plagioclase feldspars to weather more rapidly than quartz in granodiorite, and basalts to weather more rapidly than rhyolites because basalts contain more calcic plagioclases and more basic ferromagnesian minerals, and this is generally the case.

There are some complicating factors, however. Nonframework cations in biotite may weather as rapidly as olivine, resulting in physical weakening of the lattice, a commonly proposed mechanism for initiating granular disintegration of granitic rocks (Isherwood and Street 1976; Nettleton et al. 1970; Wahrhaftig 1965). The grain size of rock particles or minerals affects weathering rates. Small pieces of rock or small minerals weather more rapidly than large pieces because of their higher specific surface. For this reason, the comminution of grain sizes due to physical weathering processes may be more important in determining the actual weathering rate than the mineralogic susceptibility to chemical weathering.

METHODS OF STUDYING WEATHERING RATES

The existing literature on rates of weathering can be conveniently grouped into the following four categories: (1) descriptive field studies of weathering for Quaternary stratigraphic research, (2) watershed level studies utilizing mass balance techniques for determining nutrient budgets or chemical denudation rates, (3) tension lysimeter studies for determining nutrient budgets, and (4) laboratory studies of mineral weathering.

Geologists and soil scientists who study stratigraphic relationships of Quaternary deposits often use relative degree of weathering to distinguish deposits of different age. Weathering of individual mineral grains within a soil separate, or weathering of rocks buried in the soil or exposed on the surface can be examined. These techniques are designed to provide age correlations of deposits, often over a wide variation in climates and rock types. Using field data on weathering and absolute age control, weathering rates can be computed. Unfortunately, their weathering data are somewhat semiquantitative in nature. For example, stratigraphers might differentiate 10,000 year-old glacial till from 70,000 year-old glacial till on the basis of thickness of weathering rinds on stones found in the till. The technique works well for distinguishing between the two tills, but rarely are data provided on density changes in the weathering rind or on amounts of material weathered out. Weathering rind data can often be combined with other research on weathering to compute actual weathering rates. Estimates of weathering rates based upon Quaternary stratigraphic research merit investigation because of the diversified range of climates, parent materials, and wide geographic range of data available.

Watershed studies in which mass balances of chemical fluxes are computed can provide data necessary for computing rock weathering rates. Such studies require careful accounting of elemental inputs by precipitation and dissolved and sediment elemental losses in streamwater. Consideration must also be given to biological uptake of nutrients and soil formation. Such studies tend to be costly and require several years to adequately characterize streamflow, sedimentation, and water chemistry regimes. Data derived from such studies, however, are the most valuable for computing nutrient release rates from rock weathering.

The existing literature on mass balance studies comes from several sources. Many of the published studies have been concerned with nutrients, nutrient cycling, and plant growth. Other watershed studies have been designed to compute rates of rock weathering from a purely geochemical interest without regard for nutrients. The computation of geochemical balances as they relate to past and present geomorphology of a basin has been emphasized in some studies. Often results of these studies are presented as regional denudation rates, or rates of slope backwasting.

The approaches used by scientists in watershed mass balance studies reflect the aims of the study. Chemical denudation studies emphasize different aspects of geochemical cycling rather than nutrient release. Bedload transport rates are important to denudation studies for some rock types, and may be important to nutrient studies in that bedload transport preferentially removes smaller rock- and gravel-sized particles that are more susceptible to chemical weathering. The possible importance of this has not been studied. Rock weathering rates and nutrient gains to ecosystems computed by watershed mass-balance techniques, though not common, are becoming more frequent in the literature of geology, soils, and ecology. I examine several of these studies in this paper.

Lysimeter studies of nutrient budgets are similar in scope to watershed studies in that they require mass balance techniques to quantify gains and losses of nutrients to the system. The results are more site specific, lacking the integrating effects of a watershed scale experiment; however, there are some advantages, such as the lack of uncertainty about unaccountable deep seepage losses of nutrients in a watershed-level study. Although lysimeter studies of nutrient movement are not uncommon in the soils literature, the data required for computing rock weathering rates and nutrient release from weathering are seldom available. Data from two lysimeter studies are discussed.

Laboratory studies of elemental release under artificial weathering regimens provide useful data on mineral weathering. A broad array of minerals have been subjected to leaching regimes using dilute mineral and organic acids, plant leachates, chelating agents, and extracts from litter. Such studies have demonstrated the important role soil organic compounds play in mineral weathering. Studies of reaction kinetics and weathering rates are less common. Laboratory mineral weathering studies are discussed below.

WEATHERING RATES BASED ON FIELD STRATIGRAPHIC RESEARCH

Mineral Grain Etching

Quaternary geologists make frequent use of the degree of mineral weathering to date Quaternary deposits, to correlate deposits of similar age and to distinguish between those of differing age. Those minerals that are most susceptible to chemical weathering are most useful for dating and relative age determinations. Gradual solution of mineral grains causes their shape to become increasingly irregular with time and ultimately results in complete destruction of mineral grains. This process results in selective depletion of less resistant minerals. Birkeland (1974) has summarized data from several researchers on mineral grain etching in soils. All of these studies were concerned with establishing stratigraphic relationships of Quaternary deposits; so approximate durations of weathering are known.

Alteration of calcic plagioclase is evident in the 2-m deep soil formed from a 4000-year-old volcanic ash deposit in the British West Indies, and all calcic plagioclases have disappeared in several tens of thousands of years (Hay 1959, 1960). Although weathering in the British West Indies is rapid, Birkeland (1974) presents data to indicate that calcic plagioclase weathering rates are similar in central Europe. The central European data indicate some alteration of K-feldspars, biotite, pyroxene, and hornblende in 10^4 years.

On the California Coast (ocean terrace deposits), pyroxene etching takes more than 10^4 years; pyroxene depletion and hornblende etching take 10^5 years. Similar rates have been found for the eastern Sierra Nevada Mountains in California and the Wallowa Mountains in Oregon. Gilliam et al. (1977) presented data showing slight to moderate etching of augite and hypersthene (pyroxene minerals) grains in less than 10^4 years for soils in the San Joaquin Valley and Truckee basin, California. Depletion of these minerals takes several hundred thousand years in the same soils.

Although the above data indicate periods of from 10^3 to 10^4 years to show initial signs of weathering, we know weathering has taken place from the soils' inception; therefore, the minerals have been providing nutrients to the soil over the entire length of time until complete mineral depletion. Average rates of weathering and nutrient supply can then be calculated by knowing the chemical content of the fresh minerals, the percent of each mineral in the soil, and pro-rating weathering over the entire time interval.

Because climate has been so variable over the past hundred thousand years, any estimates derived in this manner would be quite gross. The one exception would be the Ca-plagioclase weathering rates, which showed depletion in 10^4 years. Calcium gains to that soil might be reasonably estimated knowing the Ca content of the plagioclase and the percent plagioclase in the soil.

Weathering Rinds

Weathering of rocks, boulders, tombstones, and old buildings sometimes results in formation of a weathering rind. Weathering rinds on exposed and exhumed rocks have been used extensively by Quaternary geologists for dating purposes, allowing examination of these weathering changes over time.

Birkeland (1973, 1974) presents data indicating that granitic stones on rock glacier surfaces in Colorado,. 15,000 to 20,000 years in age, have weathering rinds up to 45 mm thick and those of about 5000 years have a rind thickness of 15 mm. Volcanic rocks take longer to form weathering rinds than coarser grained plutonic rocks. Volcanic clasts at Mt. Sopris have extremely thin rinds. Colman (1977) studied weathering rinds on andesites and basalts throughout the western United States. His results indicate that rind thickness on volcanics ranges from 0.01 to 0.1 times the thickness on granitic boulders of similar age; however, he points out that the alteration may be more complete.

Tills of the youngest pre-Wisconsin glaciation, <200,000 years old, have highly weathered granitic boulders on the soil surface; boulders at depth are weathered to grus. Basalts in these same tills have rinds about 2 mm in thickness according to Birkeland (1974).

Minimum rates of subaerial weathering of granitic boulders in Sierra Nevada tills were obtained by Birman (1964) by measuring the relief between resistant aplite and pegmatite dikes and relatively easily weathered mafic inclusions in the rock. Such relief is minimal on late-Wisconsin stones, up to 7.5 cm on early-Wisconsin stones, and 15 cm on pre-Wisconsin stones.

To compute the actual volume or mass of material released by weathering during rind formation some assumptions have to be made about the density change. Fresh granitic rocks have a bulk density of from 2.65 to 2.75 g/cc, essentially equal to the weighted average solid phase density of the component minerals. For a granitic rock to preserve a weathering rind, it must not spall or crumble to grus. Clayton et al. (1979), working primarily with coarse-grained quartz monzonites and granodiorites, found that exposed granitic rocks begin to spall or grussify when their bulk densities decrease to from 2.4 to 2.5 g/cc; therefore, we might conservatively consider that the weathering rind has a bulk density of 2.5 g/cc, and estimate the starting density at 2.65 g/cc.

If we use Birkeland's figure of 15 mm as representative of weathering rind thickness for 5,000 years, we can compute the volume and mass of material weathered out for different sizes of rock. The resultant material loss is very dependent upon the size of the rock being weathered, increasing exponentially with decreasing diameter. For example, using the above assumptions and assuming a soil 1 m in depth contains 30 percent by volume granitic rock, if the average diameter of the rock is 1 m about 9 kg/ha-y of material is weathered out. These figures are graphically presented in figure 1 for particle diameters ranging from 1 mm to 1 m and for gravel or stone content of the soil ranging from 10 to 40 percent.

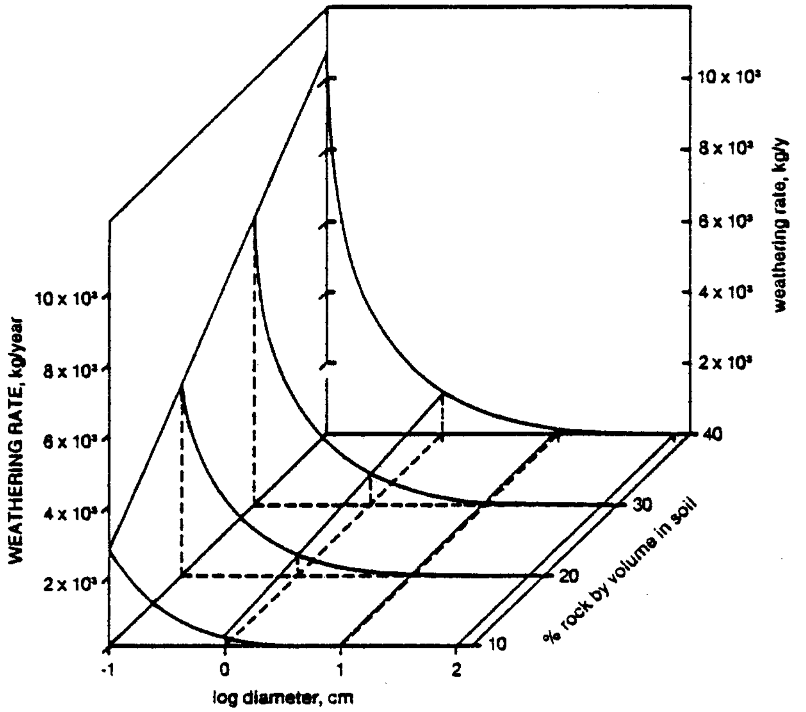

Figure 1.—The graphic relationship between particle size and weathering rate for granitic rock that makes up from 10 to 40 percent by volume of the soil. Weathering rate is expressed in kg/ha-y for a 1 meter depth of soil. The computation is based upon a weathering rind formation rate of 45 mm/15,000 y (Birkeland 1974) and a density change from 2.65 g/cc to 2.50 g/cc during rind formation.

The potential nutrient release to the soil suggested by this weathering rate computation is dependent upon what minerals are weathered during rind formation. Experience with granitic rock from the Idaho batholith suggests that weathering rind formation is similar to stage 2 weathering described by Clayton et al. (1979). This stage is characterized by hydrolysis of biotite with attendant iron and magnesium release, oxidation of ferrous to ferric iron, loss of potassium, and a gain in water. Hydrolysis of calcic plagioclases is moderate, and initial hydrolysis of alkali feldspars is mild, but evident.

Using this as a guide, and by assigning a certain mineralogy and mean particle size to the fresh gravel and rock in a soil, an elemental yield computation can be made. I made this computation for a soil located on a research watershed in the south-central Idaho batholith, using a mean gravel size in the soil of 1 cm and a mineralogy that included 30 percent plagioclase feldspar (An_{30}), 30 percent K-feldspar, and 5 percent biotite. The other 35 percent of the gravel is quartz. Further, the relative rates of weathering of the individual minerals is assumed to be 10:5:1 for biotite, plagioclase, and K-feldspar respectively. The results are presented in Table 1.

Table 1.—Elemental yield based upon weathering rind data of Birkeland 1974, mineralogical changes based upon data of Clayton et al. 1979.

Element	Mineral	Percent	Yield kg/ha-y
Na	plagioclase (An_{30})	9	52
K	biotite	2	23
	K-feldspar	19	
Ca	plagioclase (An_{30})	4	26
Mg	biotite	5	10
Fe	biotite	6	11

Although the computation of elemental yields estimated from weathering rinds was based upon some rather gross estimates, the method is sound. Further studies to clarify the actual weathering products during rind formation would improve the estimate. It should be noted that this computation was made for a young soil containing considerable fresh gravel. As the gravel weathers, the relative proportions of biotite and feldspar weathering will change. It is therefore important to define the actual weathering reactions of minerals taking place in the soil to achieve meaningful results using this technique.

Mass Balance Watershed Studies of Nutrient Gains

Mass balance studies of nutrient gains involve measurement of nutrient inputs to the ecosystem by precipitation (dry and wet) and nutrient loss from the ecosystem measured either in a stream or with tension lysimeters below the rooting zone. Measurements or estimates of biomass accrual or loss and soil nutrient aggradation are also required unless the assumption is made that soil and vegetation have reached a steady state with regard to nutrient transfer. No consideration of nitrogen fixation rates is necessary since we are only concerned with nutrients supplied by rock weathering.

A mass balance equation is then solved for the elements of concern. A typical form of this equation for calcium, expressed In kg/ha, is as follows:

Ca_{rw} = (Ca efflux - Ca influx (ppt)) + Δ Ca p+s,

where Ca_{rw} = annual calcium release from weathering, Ca efflux = annual calcium loss in a stream or lysimeter, Ca influx (ppt) =

annual calcium input by precipitation, Δ Ca p+s = annual net change in calcium accumulation in plants and soil formation (see figure 2). The sign of the parameter Δ Ca p+s is positive if there are net gains of calcium to the soil (including litter) and plants. For net losses, this parameter is ignored because we assume the losses will be accounted for in the stream efflux parameter.

In some cases, physical removal of nutrients by plant and sediment erosion must also be considered (Marchand 1974).

Seldom is the equation solved in its complete form. The plant + soil accumulation figure is often ignored, sometimes with the stated assumption that biomass and pedogenetic gains or losses are in a steady state. Often there are valid reasons for accepting the assumption of steady state, but the assumption must be evaluated on an element-by-element basis.

The relative mobility of elements released by weathering, and their tendency to accumulate either as secondary minerals in the soil or as nutrients in plants should influence the decision to measure or ignore the accumulation factor. Efflux rates of silicon, aluminum, and iron underestimate weathering rates because of the long, slow rate of secondary mineral buildup in the soil coupled with the relative immobility of aluminum and iron. In contrast, the weatering rate of the relatively mobile potassium ion will be underestimated by efflux rates principally due to biologic accumulation.

Caution should be exercised in the use of mass balance techniques to estimate weathering rates in youthful ecosystems. In such systems, the potential exists for depletion of soil nutrient reserves above amounts supplied by weathering and precipitation inputs. This is a result of rapid biomass accumulation coupled with relatively small amounts of return by litterfall and decomposition. Unless reliable estimates of soil nutrient reserves over time are available, solving the mass balance equation will overestimate rock weathering rates in rapidly developing forests.

Knowledge about the relative mobility and likely focus of elements concentrated within the ecosystem has been put to good use by several researchers in estimating weathering rates. Researchers having data on annual biomass accrual have used an element in high biologic demand to index the accumulation figure (Likens et al. 1977, Marchand 1974). Cleaves et al. (1974) used magnesium loss in the stream to index the weathering rate of serpentinite because of its relatively high mobility and the fact that supply was much greater than biologic demand. They did not have data on biomass accrual rates, but didn't need it because of the low biologic accumulation relative to release.

Several published papers on denudation rates provide a data source for rock weathering (Marchand 1971, Janda 1971, Reynolds

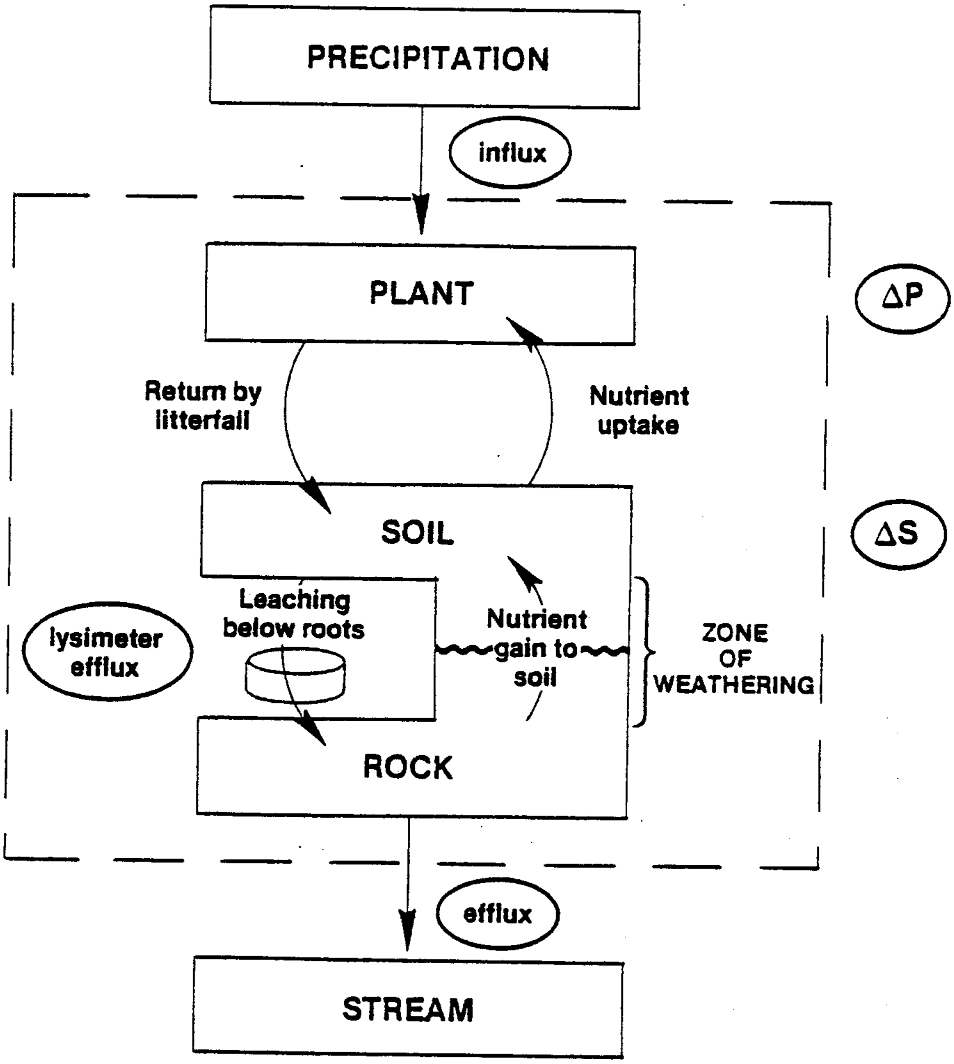

Figure 2.—Simplified diagram showing compartments (boxes) and transfer rates (arrows) required to make a nutrient budget using a mass balance technique. Nomenclature used for the rock weathering equation in the text are circled on the diagram. The wavy line between soil and rock indicates the diffuse boundary between these two compartments. Mineral weathering takes place within both compartments.

et al. 1972, Li 1976, Verstraten 1977). Denudation is the removal of material supplied from rock weathering by sediment transport and solution in a stream. Often denudation rates are expressed in units of length per time (that is, cm/1000 y) and, as such, represent the rate of lowering of the earth's crust by erosional and chemical processes.

The value of chemical denudation rate computations for estimating nutrient gains by chemical weathering generally decreases as the size and geologic complexity of the drainage basin increases.

Thus, although denudation rates for areas as large as the Amazon Basin (Gibbs 1967) or the island of Taiwan (Li 1976) are available, aside from geomorphic considerations, their usefulness is limited.

Janda (1971) pointed out that many published denudation rates are also rife with errors, the principal one being the lack of correction for atmospheric inputs to the chemical load of streams. Still, there are many excellent publications of denudation rates from small watersheds that we can use to compute rock weathering rates.

Marchand (1971) computed chemical denudation rates for a dolomite and an adamellite (quartz monzonite) parent material in the White Mountains, California. These rates were computed from the chemistry of streams draining a 538-ha basin (dolomite) and a 274-ha basin (adamellite). Chemical denudation was estimated at about 2 cm per 1000 y for the dolomite, and 0.17 cm per 1000 y for the adamellite. The chemical denudation expressed on an elemental basis, kilograms per hectare per year, for both watersheds is presented in table 2. These rates do not include accumulation figures in vegetation or soil, so they should be considered minimal values for rock weathering rates. Marchand (1974) described the relative apportionment after weathering of these elements between vegetation, colloidal exchange sites in the soil, and solution in the stream. He found that the concentration of sodium leached from the soil and entering the stream is much greater than exchangeable sodium, which in turn, is greater than sodium uptake by vegetation. Because a large proportion of the total sodium released by weathering reaches the stream, the chemical denudation rates could be adjusted by the percent sodium in the two rock types to arrive at higher, more realistic rates of nutrient release by weathering.

Verstraten (1977) published a paper on chemical denudation of a forested watershed in Luxembourg. Bedrock in this study is weakly metamorphosed shales and quartzites; the main minerals being weathered are quartz, sericite, albite, and chlorite. Total chemical denudation is 131 kg/ha-y. Annual weathering rates for Na, K, Ca, and Mg are 9, 0.2, 8.7 and 15.7 kg/ha-y, respectively (table 2). The author presents evidence to substantiate his assumption that biomass transfer of elements is in a steady state.

Fredriksen (1972) computed a nutrient budget on the H. J. Andrews Experimental Forest in western Oregon. Parent materials are volcanic tuffs and breccias of the Cascade Range. Fredriksen assumed that weathering rates offset chemical losses in the stream, and he made no corrections for biomass or soil accumulations of nutrient elements. His assumption of steady state is likely to be valid since he was working with an old growth Douglas-fir forest. Chemical dissolved losses in this study were: Na = 28, K = 1.6, Ca = 47, Mg = 11.6 and SiO_2 = 213 kg/ha-y (table 2).

Johnson et al. (1968) computed a rock weathering rate using a mass balance technique for the Hubbard Brook Experimental Forest in New Hampshire. This is a northern hardwood forest formed on

Table 2.--Comparisons of elemental release from rock weathering using mass balance techniques. All data presented in kg/ha-y. --indicates no data.

Location	Rock type	Na	K	Ca	Mg	SiO_2	Fe	Reference
White Mtns., Calif.	dolomite	2	4	86	52	32	0.06	Marchand (1971)
White Mtns., Calif.	adamellite	1	8	17	2	21.1	.03	Marchand (1971)
Cascades, Oreg.	tuffs/breccias	28	1.6	47	11.6	213	--	Fredriksen (1972)
Luxembourg	metashale	9	0.2	8.7	15.7	--	--	Verstraten (1977)
Piedmont, Md.	schist	2.6	2.3	1.3	1.7	119	--	Cleaves et al. (1970)
Piedmont, Md.	serpentinite	tr	tr	tr	34.1	55.8	--	Cleaves et al. (1974)
Hubbard Brook, N.H.	moraine/gneiss	5.8	7.1	21.1	3.5	39	--	Likens et al. (1977)
Brookhaven, N.Y.	outwash sands	6.7	11.1	24.2	8.4	--	--	Woodwell and Whittaker (1967)[1/]
RANGE		tr-28	tr-11	tr-86	2-52	21-213	0.03-0.06	

[1/] Lysimeter study.

glacial moraine material underlain by a sillimanite-zone gneiss, containing quartz, plagioclase, biotite, and lesser amounts of sillimanite. In this study, the authors assumed that rates of biomass accumulations of cations were sufficiently low to assume a steady state. The weathering rate was computed according to the method of Barth (1961), which uses dissolved chemical losses in the stream and corrects for soil accumulation and redistribution of elements during pedogenesis. Barth's equation was solved for the four cations, sodium, potassium, calcium, and magnesium, but the weathering rates determined with potassium and magnesium were rejected because they were notably lower than the rates determined from sodium and calcium data. Their best estimate of total elemental release by rock weathering at Hubbard Brook by this technique is 800 kg/ha-y.

Likens et al. (1977) recomputed the rock weathering rate for Hubbard Brook, this time taking into account the biologic accumulations of cations. They recognized that accretion of biomass resulted in a net annual storage of cations equal to 0.722×10^3 Eq/ha-y, a sizable nutrient sink. Using calcium as an index element because of its relative abundance, mobility, and biologic demand, they solved a mass balance equation and came up with a rock weathering rate of 1500 kg/ha-y. Annual release of cations by weathering using this calculation is: Na = 5.8, K = 7.1, Ca = 21.1, and Mg = 3.5 kg/ha-y (table 2). This case graphically illustrates the magnitude of the biological accumulation factor in forests that have not reached a steady state with regard to cation accumulation.

Two mass balance studies of weathering rates in the Piedmont of Maryland, (Cleaves et al. 1970, 1974) included very detailed analyses of mineralogic changes during weathering. Pond Branch watershed is forested and underlain by a schist, consisting of quartz, plagioclase, muscovite, biotite, and staurolite, with minor accessories. Soldier's Delight watershed is also forested and is underlain by serpentinite, the dominant mineral being antigorite. Based upon x-ray, petrographic, and chemical data, weathering reactions were formulated and stoichiometrically balanced to the observed water chemistry. In both studies, biomass was assumed to be in a steady state with regard to nutrient uptake and release; however, the actual rock weathering rates were indexed to elements in high supply relative to biologic demand.

For example, in Pond Branch watershed, a balanced weathering reaction for plagioclase → kaolinite is proposed, and the amount of silica and calcium released by this reaction is computed based upon sodium release. This was done because: (1) plagioclase is the only source of sodium, (2) large amounts of sodium relative to calcium (78:22) are released, and (3) sodium is minimally affected by biomass changes. Similar adjustments were made for biotite weathering.

Elemental release by weathering in Pond Branch is:
Na = 2.6, K = 2.3, Ca = 1.3, Mg = 1.7, and SiO_2 = 119 kg/ha-y

In Soldier's Delight watershed, the principal weathering reaction is hydrolysis and dissolution of antigorite:

$$Mg_3Si_2O_5\ (OH)_4 + 6CO_2 + 5H_2O \rightarrow 3Mg^{++} + 6HCO_3^- + 2H_4SiO_4.$$

Approximately half of the silicic acid released by weathering is removed by the stream water; the remainder is reconstituted into secondary minerals. Magnesium was used as an index element for this study in the same way that sodium was used in the Pond Branch study. Computed weathering release rates are: Mg = 34.1, SiO_2 = 55.9 kg/ha-y; and trace amounts of Na, K, and Ca (table 2).

Mass balance computations in Pond Branch and Soldier's Delight, when indexed to sodium and magnesium respectively, resulted in sizable accumulations of other elements. This is a result of adjusting weathering release to the more mobile index elements. Cleaves et al. (1974) grouped this residual figure into biomass plus secondary minerals plus gaseous phase losses without apportioning relative amounts.

Lysimeter Studies

Cole et al. (1967) published results of a detailed study of nutrient distribution and transfer in a second-growth Douglas-fir forest on glacial outwash in western Washington. In this study, they measured input by precipitation, uptake by trees, return to the soil by litterfall, and leaching of the forest floor, and nutrients lost from the system by leaching below rooting depth. Leaching loss was measured with tension lysimeters at a depth of 1 m.

If we use mass balance equations on their data, we can estimate the supply of nutrients from rock weathering in the same manner that watershed-level studies estimate nutrient release from weathering. Their data provide a basis for estimating elemental accumulations in both trees and forest floor. The form of the mass balance equations I used on their data is: elemental yield, weathering = (leached from soil - input by precipitation) + (uptake by tree - leached from forest floor); all data in kilograms per hectare per year.

Annual releases of K and Ca from weathering are computed at 19.2 and 8.7 kg/ha-y, respectively. These results are certainly comparable to others presented previously. I used their data on N and P in the same mass balance equation and estimated weathering releases of 33.5 and 6 kg/ha-y, respectively. Such unreasonably large releases of these two elements result from erroneously attributing the large annual accumulations in the tree and forest floor components of the ecosystem to weathering.

Much of the N accumulations in the system may be provided by fixation, but the P is probably provided by the large store in the soil, almost 60 times the amount in trees. This large store of P may reflect the relative immaturity of the forest and repeated burns by wildfires prior to reforestation. This casts some doubt on the validity of the K and Ca weathering release rates I computed from mass balance equations. In such a youthful ecosystem, weathering rates could best be estimated by indexing to an element in relatively low biologic demand, such as sodium. Grier and Cole (1972) pointed out that climatic variability also introduces a large element of uncertainty into computations of elemental transfer in developing ecosystems. During the 2-year period 1970-1971, Ca input in precipitation increased roughly 300 percent and Ca transfer by throughfall increased 600 percent over the values reported by Cole et al. (1967).

Woodwell and Whittaker (1967) reported nutrient inputs from primary mineral weathering equal to: 10.4 - 11.7 kg/ha-y K, 22.7 - 25.8 kg/ha-y Ca, 7.1 - 9.6 kg/ha-y Mg, and 2.8 - 10.6 kg/ha-y Na (table 2). These values were computed from a cation budget for the Brookhaven Forest, a mature oak-pine forest in New York. Loss of nutrients from the system was again sampled by using tension lysimeters.

Feller (1977) suggests caution in the use of tension lysimeters to estimate nutrient fluxes through soil. His objections relate to the fact that lysimeters can sample soil water from above and below the plate under certain water potentials and to the fact that macropore water may not be sampled at all.

The complex biogeochemistry of water in a plant-soil-rock-stream system may be fairly well understood in theory; however, quantification is fraught with large sampling errors related to timing of nutrient transfer and spatial variation in all components of the system. The integrating effect of a watershed level study helps to smooth such variations in time and space and is therefore preferable to lysimeter measurements when computing gross elemental release from weathering.

Laboratory Studies of Nutrient Release by Weathering

There are several studies in the literature on weathering of minerals in the laboratory by leaching with water, extracts of organic matter (Keller and Frederickson 1952), organic acids (Huang and Keller 1972, Boyle et al. 1974), mineral acids (Thompson et al. 1977), and the action of roots and microorganisms (Boyle and Voight 1973). These studies have demonstrated the importance of organic substances in accelerating the decomposition of primary minerals and transport of weathered products. In addition, rhizosphere microorganisms have been shown to accelerate nutrient release and hold nutrients within the rooting zone (Boyle and Voight 1973, Graustein et al. 1977).

Although it is hazardous to extrapolate laboratory weathering rates to rates of nutrient supply in forested ecosystems, a kinetic approach by Thompson et al. (1977) warrants further investigation. In this study, nutrient reservoirs were evaluated by continuous extraction of K, Na, Ca, Mg, and Fe with 0.5 N HCl and kinetic analysis of the extraction rate curves. Analysis of extraction rates showed up to four different rates for each element. Each rate is thought to correspond to a different type of bond site in the soil.

The amount of ion in each bond site can be computed by deconvolution of the extraction rate curve.

The authors decided that the highest extraction rates correspond to ions removed from exchange sites on colloids and that the lowest rates correspond to ions removed from primary minerals. Intermediate extraction rates result from ions removed from partly weathered minerals and organic fractions.

The available potassium reserves in the Everett soil, Cedar River Research Station, Washington, would be exhausted in a maximum of 17 years based on conventional extractable K analysis and uptake figures of Cole et al. (1967). Using their kinetic approach, Thompson et al. (1977) predict a 100-year supply of K. I would urge caution in accepting either figure as the actual potassium reserve in the Everett soil. Both figures should be considered order of magnitude estimates.

Similar studies using organic acids and chelating agents commonly found in forest soils could provide a useful technique for predicting reserves of nutrient elements released by weathering.

CONCLUSIONS

Figures on absolute rates of rock weathering are not common, but geology and soils literature can provide data from a variety of regions and climates. Predicting nutrient release from available rock weathering rates is a problem of greater concern.

Rock weathering rates based upon primary mineral grain etching and time of disappearance of particular minerals in soil must be considered of limited value because of the long time periods (10^4 to 10^5 years) before recognizable weathering takes place. This is the case even for relatively easily weathered minerals of small particle size. Known climatic fluctuations over these time periods suggest that predictions of current weathering rates based upon long-term mineral grain etching are unlikely to be accurate. The one exception may be weathering in soils of calcic plagioclase, which has been shown to weather extensively in 10^4 years in both central Europe and the British West Indies. Computing Ca release from this rate of plagioclase weathering, though gross, may be considered a somewhat reliable best estimate when no other data are available.

Estimates of nutrient release based upon thickness of weathering rinds present similar problems to estimates based upon mineral grain etching. Although the zone of weathering may be accurately portrayed by a suitable sample of rind thickness measurments, we know little about the actual amount of material released. These estimates will improve when we have data on bulk densities and mineralogical changes during rind formation. The potential effects of climatic change over long periods of time necessitate caution in using weathering rind data on deposits older than 10,000 years.

The effects of cold climates on rate of chemical weathering may be more complicated than we previously thought. We generally expect the rate to go down as temperature decreases; in harsh glacial environments, the rate of chemical weathering has been considered to be very low. Reynolds and Johnson (1972) found chemical denudation rates from waters draining a glacier in the northern Cascade Mountains to be three times the world average for temperate basins. Apparently the low temperature effects were offset by comminution of rock by ice grinding, which accelerated chemical weathering in this study. Birkeland (1973) also indicated that rates of chemical weathering do not decrease in the alpine climate above tree line in the Rocky Mountains of Colorado.

These studies emphasize the fact that relationships beween chemical weathering and climatic regime are not well understood. Differences in weathering rates between cold and temperate climates may be quite small.

Mass balance nutrient studies provide the best estimates of nutrient release from rock weathering, but the published studies vary widely in their approach and attention to detail. The most complete studies include accurate assessment of nutrient sources and sinks and of proposed chemical reactions for weathering of minerals. Such studies require sound data on net biomass accumulations of nutrients, nutrient gains to the soil, and consideration of differential weathering rates of minerals, in addition to data on precipitation inputs and losses in water. The complex geochemistry of weathering reactions coupled with the complex cycling between soil and plants indicates that transfer rates of nutrients between all points in the biogeochemical system must be considered to quantify rock weathering rates. Of the studies reviewed in this paper, those by Marchand (1974), Cleaves et al. (1970, 1974), and Likens et al. (1977) most completely fit these requirements.

The principal drawbacks to mass balance studies of nutrient flows are the time and costs involved. Long-term hydrologic and meteorologic data are required for watershed-level studies and such data are costly. Temporal variations in chemical fluxes are generally more stable than hydrologic and climatic regimes, but relationships between water yields and chemical fluxes must be established. This involves careful sampling of extreme events.

Similar problems exist for lysimeter level studies. Grier and Cole (1972) pointed out the magnitude of difference in chemical influx from precipitation from year to year. Annual variations in elemental loss below the rooting zone are similar to variations observed in stream water. The credibility of lysimeter estimates of nutrient release is also enhanced by long-term studies.

Laboratory studies of mineral weathering require much less time and are less costly as well. Laboratory research does not suffer at the mercy of climatic irregularities, and sampling is greatly simplified. The principal drawback to laboratory simulations of weathering is a lack of demonstrable extrapolation to the field. Laboratory simulations of weathering that best mimic field weathering include judicious use of acids and organic components that are found naturally in soils. Simulating microbiological influences is more difficult, but not impossible. As laboratory studies become more common, comparisons with field research should provide a basis for judging their accuracy.

One element that deserves further discussion is phosphorus. Phosphorus release rates from weathering are difficult to determine because of the lack of mobility of this element. Most mass balance studies in which phosphorus has been analyzed indicate very small losses from the system, generally equaled by small inputs from precipitation. Phosphorus released from weathering of primary minerals is tied up in the plant-soil system, and the great majority of this is in the soil. About half the phosphorus in soil is contained in organic compounds such as phytin, phospholipids, and nucleic acids. The inorganic half is tied up in very immobile iron, aluminum, and calcium compounds and in clay minerals. Trees require inorganic orthophosphate for their nutrition. Rates of supply of phosphorus in this form are largely dependent upon microbial transformations of phosphorus and ionic activities of Ca, Al, and Fe. As such, weathering rates of primary minerals containing phosphorus may be relatively unimportant for supply of this nutrient to trees. The potential for depleting phosphorus reserves by intensive harvesting may be less damaging than the potential depletion of the more mobile (and less abundant) K and Ca reserves in soil.

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