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Rapid, plant-induced weathering in an aggrading experimental ecosystem

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Abstract. To evaluate whether rates of weathering of primary minerals are underestimated in watershed mass-balance studies that fail to include products of weathering accumulating in plants and in developing soil, changes in the calcium and magnesium content of vegetation and soil fractions were measured in large, monitored lysimeters (sandbox ecosystems) at Hubbard Brook Experimental Forest, New Hampshire. Weathering was evaluated over 4–8 yr in sandboxes planted with red pine (*Pinus resinosa* Ait.) and kept mostly free of vegetation (nonvegetated). Three mass-balance equations were used that cumulatively include (a) Ca and Mg in precipitation inputs and drainage outputs, (b) accumulation of Ca and Mg in vegetation, and (c) changes in products of weathering in soils. Soil products were evaluated with an extraction process designed to avoid removing ions from primary minerals. Relative to the input-output equation, the estimated rate of weathering increased 2.4 (Ca) and 1.8 (Mg) times when accumulation of Ca and Mg in pine biomass was accounted for, and 8 (Ca) and 23 (Mg) times when changes in soil products were also included. Weathering estimates that included accumulation in vegetation and soil products were 261 (Ca) and 92 (Mg) kg ha^{-1} yr^{-1} in the pine sandbox. These rates were 10 (Ca) and 18 (Mg) times higher than the rates in the nonvegetated sandbox, which were not significantly greater than zero. This study raises the possibility that weathering can play a significant role in the release of nutrients available to plants over short periods. Faster rates like this become extremely important where managers are trying to balance nutrients available to plants from precipitation and weathering release with outputs including harvest removals.

Key words: cations, denudation, ecosystems, nutrient availability, sustainability, weathering

Introduction

Nutrients required for plant growth, other than nitrogen and sometimes sulfur, are initially supplied by the chemical dissolution of primary minerals in the process known as weathering. Silicate minerals weather when mineral surfaces come in contact with hydrogen ions, usually donated from the dissolution of carbon dioxide in water. Secondary minerals, cations, and bicarbonate are important products (Holland 1978):

$$2CO_2 + 3H_2O + CaAl_2Si_2O_8 = Al_2Si_2O_5(OH)_4 + Ca^{2+} + 2HCO_3{}^{-}. \quad (1)$$

Hydrogen ions from the dissolution of organic acids, such as oxalic acid, also can weather silicate minerals, but without a bicarbonate product:

$$H_2C_2O_4 + H_2O + CaAl_2Si_2O_8 = Al_2Si_2O_5(OH)_4 + CaC_2O_4. \quad (2)$$

Thus, passively through respiration and actively through release of acids, weathering is promoted by bacteria (Schwartzman & Volk 1989; Hiebert & Bennett 1992), even in groundwater (Hiebert & Bennett 1992); fungi (Henderson & Duff 1963; Moira et al. 1963; Silverman & Munoz 1970), lichens (Krumbein 1983); higher plants (April & Keller 1990; Hinsinger et al. 1992; Arthur & Fahey 1993; Berner 1995); and especially symbiotic and associative combinations of organisms (Leyval et al. 1990; Griffiths et al. 1994). Mechanisms for active, biologically mediated chemical weathering include secretion of organic acids (Boyle et al. 1974; Graustein et al. 1977). In essence, higher plants and their associates speed weathering through release – associated with root growth, exudation, and turnover – of carbonic and organic acids in close proximity to primary minerals which tend to be more abundant deeper in the soil. Minimally vegetated ecosystems generally have little or no decomposable soil organic matter and therefore rely on carbonic acid in rainfall and on microbial respiration near the soil surface to drive weathering.

Knowledge of how species and assemblages of species affect weathering is important to understanding long-term productivity, ecosystem development strategies, and global C cycling. Young, aggrading ecosystems have increased demand for, and uptake of, nutrients (Bormann & Likens 1979; Gorham et al. 1979), suggesting that capacity to enhance weathering might be important in pioneer and early-successional species. Phosphorus, Ca, and Mg are often thought to become limiting in the later stages of ecosystem development (Tiessen et al. 1994), perhaps reflecting reduced weathering ability by species associated with later stages. Recurring harvest removals and leaching losses of Ca from northern hardwoods can exceed estimated precipitation inputs and weathering, possibly leading to reduced productivity (Federer et al. 1989; Likens et al. 1996).

Rates of chemical weathering in ecosystems and release of base-element nutrients are often perceived to be slow, with noticeable change only after centuries or longer (NRC 1994). This perception is based on estimates of weathering rates, mostly from small-watershed studies applying an equation that balances loss of base elements from primary minerals inside the ecosystem boundary ($-\Delta$*primary minerals*) against net drainage loss (*drainage* $-$ *precipitation*):

$$-\Delta primary\ minerals - (drainage - precipitation) = 0. \tag{3}$$

Use of this equation makes weathering equal to net drainage loss (also called chemical denudation) by assuming that other changes in storage do not occur, for example that vegetation and soils are in a steady state.

Watershed mass balance studies have produced important information, mostly on chemical denudation. Net release of Ca, for example, ranges from a trace in areas underlain by Ca-poor serpentinite (Cleaves et al. 1974) to 86 kg ha^{-1} yr^{-1} in watersheds containing Ca-rich dolomite (Marchand 1971). Many of these effects can be connected to specific mineral weathering reactions (Johnson et al. 1968; April & Newton 1992). Vegetation also alters the rate of denudation on similar parent materials; for example, on monzonitic granite, calcium denudation was estimated to be 11 kg ha^{-1} yr^{-1} for a spruce ecosystem, 7 kg ha^{-1} yr^{-1} for a grassland, and 3 kg ha^{-1} yr^{-1} for a beech coppice (Lelong et al. 1990). Total mass of Ca and Mg in non-exchangeable soil pools declined 42 (Ca) and 29 (Mg) % faster under Coulter pine than under scrub oak (Quideau et al. 1996).

Limits to knowledge of weathering rates lie primarily in the inadequate quantification of base-elements accumulating in vegetation and as weathering products in soil during soil development. Although some watershed studies account for accumulation in vegetation (Likens et al. 1977; Lelong et al. 1990), many do not (e.g., Marchand 1971; Fredriksen 1972; Cleaves et al. 1974; Verstraten 1977; Clayton & Megahan 1986). Nutrient element budgets (e.g., Sollins et al. 1980) can account for changes in mass of live vegetation, coarse woody debris, and soil organic matter, but generally do not account for changes in mineral soil. Direct measures of soil-product accumulation require long-term studies to produce empirical evidence, and few such studies are available. Because of large horizontal and vertical variability of soils in watersheds, detecting changes in the proportion of primary mineral mass to total soil mass or changes in quantity of secondary minerals during short periods of weathering is extremely difficult.

Small-scale experimental ecosystems allow more quantitative assessments of process rates than do small-watershed studies (Bormann et al. 1987; Bormann et al. 1993; Quideau et al. 1996). They can be constructed so that inputs, outputs, and changes in storage can be carefully and less-expensively monitored, while maintaining a vigorous, stand-scale plant cover. We applied this method to examine rates of weathering by measuring products of weathering left in soil (*products*); living plants, including live roots and litter (*vegetation*); and inputs and outputs of base elements. This method can determine potential ecosystem weathering rates, but may not represent more complex large-scale ecosystems.

Weathering in our ecosystem is considered an internal process that transfers base elements from the primary-mineral pool initially to *vegetation* and *products* pools. *Products* are collectively defined as base elements in soil solutions, on exchange sites, and in living and dead soil organic matter (exclusive of live roots), amorphous residues, and secondary minerals. Amorphous residues are generally thought to be poorly structured hydroxides, hydrous oxides, and oxides of iron, aluminum, and manganese; they include, for example, thin films of aluminum hydroxide, streaks of ferric hydroxide, and discrete colloidal particles (Russell 1973).

Losses of base elements in primary minerals ($-\Delta$*primary minerals*) balanced by the changes in storage, vegetation accumulation (Δ*vegetation*) and products of weathering left in soil (Δ*products*), and estimates of net drainage loss from drainage losses (*drainage*) minus wet and dry inputs in bulk precipitation (*precipitation*) constitute a mass-balance equation free from steady-state assumptions:

$$\begin{aligned}&(-\Delta primary\ minerals - \Delta vegetation - \Delta products) - \\ &(drainage - precipitation) = 0.\end{aligned} \tag{4}$$

When weathering is defined as the loss of base elements from primary minerals in the ecosystem ($-\Delta$*primary minerals*), the equation can be rearranged to calculate weathering. Because different authors and disciplines define weathering in different ways, we compare three equations for estimating weathering:

$$weathering = drainage - precipitation, \tag{5}$$

$$weathering = drainage - precipitation + \Delta vegetation, \text{ and} \tag{6}$$

$$\begin{aligned}weathering = drainage - precipitation + \Delta vegetation + \\ \Delta products.\end{aligned} \tag{7}$$

Equation 5 assumes no change in base-element pools in vegetation or soil products; equation 6 assumes that base elements accumulate only in vegetation, not in soil products; and equation 7 includes soil products. Because Δ*vegetation* and Δ*products* are positive components of the equation, actual weathering is higher when these components are included; the opposite holds if *precipitation* does not include impaction inputs.

In this paper, we seek to estimate weathering rates for experimental ecosystems with and without vegetation to better understand the effect of plants on the rate of weathering and soil and ecosystem development. Because of the methods used, we focused on weathering release of Ca and Mg over 4 to 8 years. We evaluate the following hypotheses: (a) the terms Δ*vegetation* and Δ*products* are large and positive, which results in higher estimates of weathering (rates in equation $7 > 6 > 5$); and (b) weathering in our experimental ecosystems with vigorous plant growth is more rapid than in nonvegetated ecosystems.

Methods

We report here weathering data from mesocosms, called "sandboxes," designed to represent simplified natural ecosystems. Sandboxes were constructed on the Hubbard Brook Experimental Forest in central New Hampshire, and have been described before (Bormann et al. 1987; Bormann et al. 1993). Soil in the sandboxes is a 15 cm layer of local water-washed stones, 1.9–3.8 cm in diameter covered by 1.3 m of 0.95 cm screened and homogenized glacial outwash of granitic and metamorphic origin. This "sand" material was obtained from about 10 m deep in a glacial outwash deposit near the Pemigewasset River by a local sand and gravel company, and contained glacially ground sand and smaller-sized rock particles. To enhance the survival of seedlings, 5 cm of mixed topsoil, previously removed from the original surface, was added to the sandboxes and incorporated into the upper 20 cm of the sand layer by several passes with a rototiller. For this study, two large sandboxes (7.5 × 7.5 m wide × 1.5 m deep) with monitored drains – planted with red pine or kept largely free of vegetation – and one small unmonitored red pine sandbox (2.5 × 2.5 m wide × 1.5 m deep) were used to evaluate the terms: *drainage, precipitation*, Δ*vegetation*, and Δ*products*. Approaches to measuring and interpreting these terms follow.

Mineralogy

Mineralogy of samples of the original outwash sand, topsoil, and initial sandbox soil (0–5, 10–20, 30–40, and 50–60 cm) was determined by x-ray diffraction and optical petrographic and scanning electron microscopy. For x-ray diffraction analysis, aliquots of soils were comminuted in a tungsten carbide grinding dish. Random powder mounts of the samples were prepared and then analyzed for the presence of major and minor minerals on a Diano 8535 semi-automated x-ray diffractometer fitted with a Cu-tube. Scans were run using Ni-filtered, CuKα radiation produced at 45 Kvp and 15 milliamps, and a goniometer slew rate of 2 degrees, 2θ per minute. Sample preparation and analytical techniques for clay minerals generally followed the scheme of Jackson (1974). Soil samples were washed through a 230-mesh stainless steel sieve, mechanically disaggregated by sonification, and the $<2\mu$m fraction was isolated by centrifugation. The x-ray powder diffraction analyses were performed on oriented powder mounts using Ni-filtered, CuKα radiation, a 1-degree beam slit, medium resolution soller slit, and a 0.1-degree receiving slit.

Samples were also analyzed for light and heavy mineral content. Separate aliquots of sandbox soil were dry sieved into light and heavy mineral fractions by using tetrabromethane (specific gravity of 2.96) and prepared for inspection under the petrographic microscope. Both light and heavy mineral slide mounts were prepared by mounting the fine to very-fine sand fractions in epoxy. The slide was then ground down to optical thickness (0.03 mm) and polished. Ribbon point counting of about 300 grains per slide – using both optical and scanning electron microscopes – provided data on grain frequencies of mineral species (e.g., hornblende, biotite, plagioclase, K-feldspar). The same slides were also used to determine mineral chemistry on a JEOL Superprobe (electron microscope, SUNY, Binghamton). The slides were ultra-polished, carbon coated, and then mounted in the electron microscope where selected light and heavy mineral grains were analyzed for 10 elements. Each grain was analyzed at least twice, at different X-Y coordinates, and these results were used to produce an average chemical composition for each mineral species. These analyses were then recast into structural formulae.

Net drainage loss

Drainage. We estimated Ca and Mg in drainage from the sandboxes based on interpolated estimates of concentrations and flow. Samples for chemical analyses were taken approximately weekly during the period of active drainage, for a total of 120 samples during 1984–1988. Instantaneous flow out of the boxes was measured at intervals usually ranging from 1 to 7 days. From 1984–1988, more than 600 observations were made during times when drainage was actively flowing (excludes winter and late summer; the red pine box usually ceased draining in June or July, but one year stopped as early as the end of April). Interpolated daily flow was multiplied by interpolated daily concentrations to yield daily flux. These values were summed for the study period.

Precipitation. Input of Ca and Mg in bulk precipitation was measured weekly in a nearby Hubbard Brook long-term biogeochemistry monitoring station from 1983–1988 (D. Buso, Hubbard Brook Experimental Forest, West Thornton, NH, pers. comm.). Our *precipitation* measure includes dust that settled in an open collector; some fine dusts and aerosols collecting on leaves were likely not measured (Lovett & Lindberg 1986). We assumed that other inputs and outputs (e.g., insects, wind-blown litter) were insignificant. Fog drip is inconsequential on this low-elevation site (Weathers et al. 1988). Unfiltered bulk precipitation samples were analyzed for Ca and Mg concentration by atomic absorption spectrophotometry as described by Bormann & Likens (1967).

Accumulation in vegetation and litter

Red pine seedlings of known weight and chemical composition were planted June 6, 1983. Some replanting of failed seedlings was required. Weeds were pulled and dropped in place several times during the first few years. No dead seedlings or weeds, or the Ca and Mg they contained, were removed from any of the sandboxes. A buffer of three or six rows of seedlings at the same spacing was planted outside of the small and large sandboxes, respectively. All seedlings had a soil growing space of 0.25 m^2, except for those planted adjacent to the sandbox walls. Because the position of the walls did not match the spacing of the seedlings, the row just inside the wall had a soil growing space of 0.38 m^2, and the row just outside the wall had a soil growing space of 0.13 m^2. The central four of the 16 red pine trees in a small sandbox were harvested during August and September 1988 to determine change in storage of Ca and Mg in vegetation above ground. Height growth of border trees was not statistically different ($p > 0.05$, t-test) from nonborder trees (Bormann et al. 1993).

Trees were cut 5 cm above the soil surface and separated into foliage, branch, and stems. Root samples, obtained while processing soil samples, were divided into <2 mm and >2 mm diameter fractions. Stumps included 5 cm of stem above the soil surface and a 5 cm length of each root attached to the root stock. Herbs, grasses, and mosses were collected from the aboveground growing space (0.25 m^2) associated with each sampled tree and processed like the other biomass samples (Bormann et al. 1993). Litter, treated as part of the vegetative component because it was not present initially, was collected from the 0.25 m^2 space under all of the six sampled trees. Minor amounts of litter were blown into and out of the sandboxes. We assume that these were roughly equal or otherwise insignificant to the Ca and Mg budgets. After oven drying (65 °C), samples were finely ground in a large blender or Wiley mill. Stem segments and stumps were randomly subsampled before being ground. A single proportional composite sample was constructed for each component: foliage, branches, stems, and reproductive parts. Tissue and litter samples were digested (0.1 g tissue, 1.5–2 h, 450 °C, Technicon BD-

40, with 75 ml reflux tubes) using sulfuric acid and hydrogen peroxide as oxidizers, selenium as a catalyst, and lithium sulfate to elevate the boiling point (Parkinson & Allen 1975). Solutions were analyzed for Ca and Mg by using ICP-AES (Thermo Jarrell-Ash).

To determine average annual rates of change, we divided changes in storage and inputs and outputs by appropriate time intervals. For vegetation and litter, we used the decimal years between planting and harvesting: 5.2 yr for red pine. For soils, we used the time since initial soil sampling, September–October 1984, to the final sampling: 3.8 yr for red pine and 7.8 yr for the nonvegetated sandbox.

Change in weathering products left in soils

Our approach to measuring soil changes was based on the premise that detecting changes in Ca and Mg Δ*products* pools (soil solution and exchange sites, soil organic matter, transition metal oxyhydroxides, amorphous Al and Si compounds, and secondary minerals) is easier than detecting changes in the much larger primary mineral pool in this glacial-origin soil material. This premise was supported when no statistically significant differences between mass of primary minerals of initial 1983 sand and samples taken in 1988 were found. We define the changes measured in non-primary mineral or Δ*products* pools as the changes in the amount of Ca and Mg that can be extracted with the method developed by Rozan et al. (1997).

To establish initial soil conditions, 0–10 and 10–20 cm cores were removed from all sandboxes with a piston-type soil corer, 5.3 cm in diameter (Bormann et al. 1993) during autumn 1984. Sixteen to 18 cores were collected from each sandbox at randomly selected points, farthest from seedlings. To minimize soil compaction during coring, walking in the sandboxes was limited to boards placed on the soil surface. The exact location of each core was recorded and holes created by coring were back-filled with initial sand. Cores were expelled directly from the corer into previously weighed and labeled 177-ml flint-glass jars. Jars with soil were ovendried to a constant weight at 65 °C and then sealed and stored for future chemical analyses. We removed five deep cores to depths of 50–75 cm from the nonvegetated sandbox in October 1985. Core sections could not be retrieved from deeper depths, and no initial cores were taken below 20 cm in vegetated sandboxes. The Ca and Mg contents of deep cores were indistinguishable from grab samples of bulk sand before it was added to the sandboxes; thus, we assumed that initial deep cores in the nonvegetated sandbox were representative of the deep soil layers in the other sandboxes. Use of the deep-soil Ca and Mg content in the nonvegetated sandbox for initial conditions in the red pine sandboxes is discussed in Results. Initial samples of soil were not collected until one year after seedlings were planted.

Final soil conditions in the nonvegetated sandboxes were measured using cores following the procedure for initial samples. Cores were taken from random locations in the nonvegetated sandbox. Final soil conditions in the small red pine sandbox were established by sampling the entire growing space (0.25 m^2) below each of the four central trees to avoid possible edge effects of the sandbox walls. The upper 30 cm of mineral soil was collected with a $0.50 \times 0.50 \times 0.32$ m open-ended frame made from four 6.3-mm-thick steel plates welded together and sharpened on the bottom. This sampler, centered around each stump, cut through the large roots that had developed and encompassed effects of rooting and stem flow associated with tree position. Four mineral soil layers were collected: 0–5 cm; 5–10 cm; 10–20 cm; and 20–30 cm. Entire-layer samples were first sieved through 6.35-mm hardware cloth to remove larger roots and coarse fragments. A subsample (8–25% of total wet weight) of the remaining soil was obtained with a riffle subsampler. The subsample was further divided into fine earth (<2 mm) and small coarse fragments (2–6.35 mm). Small root fragments missed in the first sieving were meticulously separated from these subsamples. The 5.3-cm-diameter corer was used to collect 10-cm core sections from 30 cm to the bottom of the sandbox (1.35 m) at one point under each tree. These samples were used for soil analyses, but not root biomass. After coring, a 0.25 m^2 monolith was excavated to a depth of 1 m to collect remaining deep roots. Soil samples were airdried for several weeks and then ovendried. Nutrients in soil samples were analyzed on material dried to 65 °C, but results are based on a 105 °C dry weight.

Soil mass was calculated (1) using both initial core samples and final samples from box samplers to 30 cm and deep cores, and (2) using only the final samples and assuming that soil mass did not change during the study. These methods yielded small but significant ($p < 0.05$) differences in soil mass that we could not separate from a sampling bias (Bormann et al. 1993). Method 1 produced slightly higher estimates of Δ*products* and of weathering rates, and thus we chose the more conservative method 2.

To measure changes in the Δ*products* pool, we used the method of Rozan et al. (1997), where Ca and Mg were brought into solution leaving primary minerals intact. Duplicate or triplicate extractions of 5-g subsamples were analyzed by inductively coupled plasma, atomic emission spectrophotometry (ICP-AES). The preservation of primary minerals during the extraction was assessed with two independent methods. In the first, pure samples of representative primary minerals (plagioclase, potassium feldspar, hornblende, and biotite) were extracted to assess dissolution. These minerals account for 93%

of non-quartz minerals in the sandbox soil and have more easily weatherable matrices than does quartz. The second method used Rb as a trace indicator. Rubidium is abundant in primary minerals, especially feldspars, but it is scarce in the secondary minerals found in our soil. Therefore, when rubidium was found in extracted solutions in more than trace amounts, primary minerals were assumed to have been destroyed. Both assessments found only trace amounts of Rb (less than 0.4% dissolution). Furthermore, because both initial and final soil samples were subject to the same procedure, the error is much lower than this percentage. Partial solubilization of primary minerals would lead to overestimates of weathering rates because unweathered minerals are present in much greater quantities than are weathering products. Formation of extraction-resistant secondary minerals, which could cause underestimation of weathering rates, was assumed to be negligible.

Statistical analyses

The variance of each term in equation 7 was determined to allow a combined error estimate for weathering rates. The available data sometimes did not have the characteristics of a standard normal variate, and the potential error was estimated instead. The total error was summed assuming each term was statistically independent and errors were random. The rationale for developing variance estimates for each term is discussed below.

Drainage flux of Ca and Mg was estimated from daily interpolated values of flow and concentration. This approach allows no statistically rigorous method of estimating error variance. Conservatively, the flux bounds were calculated from using the annual low and high concentration values (average of the 10% lowest and highest values) times the estimated annual drainage. Establishing these bounds as the 95% limits permits a very crude, but conservative, estimation of an independent error that can be combined in the summary weathering equation.

Bulk precipitation inputs were estimated from the Hubbard Brook monitoring station about 200 m from the site. This single station allows no estimate of sample variance. Measurement error is likely to be substantially smaller than sampling error. Because the input values were so much smaller than the other terms in equation 4 and no actual measurements of sampling error were available, no variance contribution was entered for this term.

Mean and standard error of initial seedling biomass was estimated from dry weight of random samples from the population being planted. The initial biomass and nutrient content were much smaller than the sampling error at the end of the experimental period. For the final estimate of accumulated biomass and nutrients in the red pine sandbox, the portions above and below the ground of all four plants in the center of the sandbox were harvested.

Initial soil samples were collected randomly across the sandboxes by using a coring device. Final soil samples represented the entire 0.25 m^2 growing space beneath each of the sampled trees for the depths from 0 to 30 cm. Below that depth, the coring device was used. Thus, for 0–30 cm depths, the final sampling represents a 100% sample of the material needing evaluation and, below 30 cm, only a partial sample. For both depths, a simple mean and standard error were calculated.

Results

Mineralogy

Minerals identified in the sandboxes are arranged into light minerals with specific gravity less than 2.96 and heavy minerals with specific gravity greater than 2.96 (Table 1). A second division separated minerals by particle size into two classes, clays (less than 2 μm) and larger particles greater than 2 μm.

Light minerals. The light minerals – including quartz, feldspars, and muscovite – make up about 90% of the sandbox soil (0–130 cm). Light minerals are generally more resistant to weathering than are heavy minerals. Among the light minerals, quartz is relatively nonreactive in soil weathering reactions; plagioclase and K-bearing feldspars weather more readily. The plagioclase feldspars produce a solid solution series ranging from albite (Ab_{100}, $NaAlSi_3O_8$) to more readily weatherable anorthite (An_{100}, $CaAl_2Si_2O_8$). Plagioclase composition of the sandbox averages An_{23} (i.e., 23 molecular% anorthite, the calcium-rich end member and 77 molecular% albite, the sodium-rich end member). Muscovite is a K-rich phyllosilicate that, along with the K-feldspars, is moderately resistant to chemical alteration.

Heavy minerals. The heavy minerals, about 10% of the sandbox soil, include a wide variety: the oxides ilmenite and magnetite, amphiboles, pyroxenes, garnet, epidote, apatite, biotite, chlorite, and others (Table 1). Some heavy minerals – such as ilmenite, magnetite, zircon, sillimanite, and rutile – are resistant to chemical attack; others – such as pyroxene, hornblende, apatite, and garnet – are reactive and can account for a disproportionately high percentage of the base elements released by weathering into the soil solution. As expected, heavy minerals make up a smaller fraction (3%) of the initial 5 cm of topsoil, likely a result of post-glacial weathering of heavy relative to light minerals.

Table 1. Abundance of light and heavy (bolded) primary minerals in initial sandbox soils (0–135 cm) and their total base-element content; footnotes are weathering reactions that contribute base elements in the approximate order of ease of weathering.

		Ca	Mg
Primary mineral	Wt.%	Mg ha^{-1}	
Quartz	41	0	0
Ca Na plagioclase	17	128	0
Albite	11	0	0
K feldspar	8	0	0
Perthite	8	0	0
Muscovite	4	0	0
Hornblende[4]	2	35	30
Biotite	2	0	15
Fe oxide	1	0	0
Clinopyroxene[1,3]	1	20	17
Ilmenite	1	0	0
Epidote[7]	1	24	0
Garnet[9]	1	1	1
Chlorite	trace	0	4
Actinolite[5]	trace	6	7
Apatite[8]	trace	26	0
Staurolite	trace	0	0
Sphene[6]	trace	8	0
Zircon	trace	0	0
Orthopyroxene[2]	trace	trace	3
Rutile	trace	0	0
Kyanite, andalusite, or sillimanite	trace	0	0
Total	100	248	78

[1] Clinopyroxine 1 (Augite): $Na_{0.04}Ca_{0.65}Mg_{0.72}Fe_{0.39}Al_{0.14}Si_{1.99}O_{6(s)} + 2.45H^{+} + 3.16H_{2}0 \rightarrow 0.04Na^{+} + 0.65Ca^{2+} + 0.72Mg^{2+} + 1.99H_{4}SiO_{4} + 0.39FeO(OH) + 0.14Al(OH)_{3}$

[2] Orthopyroxene (Hypersthene): $Mg_{0.95}Fe_{0.75}Si_{2.11}O_{6(s)} + 1.31H^{+} + 3.94H_{2}O \rightarrow 0.95Mg^{2+}$ $2.11H_{4}SiO_{4} + 0.75FeO(OH)$

[3] Clinopyroxene 2 (Diopside): $Na_{0.03}Ca_{0.58}Mg_{1.03}Fe_{0.18}Al_{0.09}Si_{2.02}O_{6(s)} + 3.11H^{+} + 2.71H_{2}O \rightarrow 0.03Na^{+} + 0.58Ca^{2+} + 1.03Mg^{2+} + 2.02H_{4}SiO_{4} + 0.18FeO(OH) + 0.09Al(OH)_{3}$

[4] Hornblende: $(K_{0.1}Na_{0.41}Ca_{1.8})(Mg_{2.54}Fe_{1.72}Mn_{0.05}Ti_{0.07}Al_{0.7})Si_{6.88}Al_{1.12}O_{22}(OH)_{s(s)} + 7.86H^{+} + 12.42H_{2}O \rightarrow 0.1K^{+} + 0.41Na^{+} + 1.84Ca^{2+} + 2.54Mg^{2+} + 0.05Mn^{2+} + 0.07Ti^{4+} + 6.88H_{4}SiO_{4} + 1.72FeO(OH) + 1.82Al(OH)_{3}$

Table 1. Continued.

[5] Actinolite: $(K_{0.03}Na_{0.09}Ca_{1.94})(Mg_{3.66}Fe_{0.91}Mn_{0.1}Ti_{0.01}Al_{0.27})Si_{6.88}Al_{0.21}O_{22}(OH)_{2(s)} + 10.67H^+ + 10.42H_2O \rightarrow 0.03K^+ + 0.09Na^+ + 1.94Ca^{2+} + 3.66Mg^{2+} + 0.1Mn^{2+} + 0.01Ti^{4+} + 7.79H_4SiO_4 + 0.91FeO(OH) + 0.48Al(OH)_3$

[6] Sphene: $CaTi(SiO_4)OH + 4H^+ \rightarrow Ca^{2+} + Ti^{4+} + H_4SiO + OH^-$

[7] Epidote: $Ca_2Al_{2.26}Fe_{0.81}Mn_{0.01}Si_{3.14}O_{12}(OH)_{(s)} + 3.23\ H^+ + 7.96H_2O \rightarrow 2Ca^{2+} + 0.01Mn^{2+} + 3.14H_4SiO_4 + 2.26Al(OH)_3 + 0.81FeO(OH)$

[8] Apatite: $Ca_5(PO_4)_3(OH)_{(s)} \rightarrow 5Ca^{2+} + 3(PO4^{3-}) + OH^-$

[9] Garnet: $Ca_{0.18}Mg_{0.3}Fe_{2.03}Mn_{0.31}Al_{2.07}Si_{3.05}O_{12(s)} + 15.5H^+ + 2.47H_2O \rightarrow 0.18Ca^{2+} + 0.3Mg^{2+} + 0.31Mn^{2+} + 2.03FeO(OH) + 2.07Al(OH)_3 + 3.05H_4SiO_4$

Minerals in the clay fraction. Clay minerals in soils are either inherited from the parent material or are formed from the weathering of primary minerals through solid state transformation, or by precipitation from the soil solution. Clay minerals – making up less than 2% of the bulk sandbox soil (both topsoil and outwash sand) – were identified as mica (illite, muscovite, and biotite), vermiculite, kaolinite, smectite, and mixed-layer clays.

Components of the weathering equations

Four components – drainage losses, precipitation inputs, vegetative uptake, and changes in the products of weathering in soil – are considered separately before being combined in equations 5–7:

Drainage losses **(drainage).** Losses from the red pine sandbox averaged 34 (Ca) and 4 (Mg) kg ha^{-1} yr^{-1}; losses from the nonvegetated sandbox were similar, 35 (Ca) and 4 (Mg) kg ha^{-1} yr^{-1}, even though concentrations were very different (Figure 1). As leaf area and evapotranspiration increased in the red pine sandbox during the first year, water drainage – as a percentage of precipitation – declined. For example, in 1983, drainage was about 70% of precipitation in red pine and 90% of precipitation in the nonvegetated sandbox. This percentage declined to a low of about 20% for the red pine in 1986 but remained constant in the nonvegetated sandbox. Losses of Ca and Mg, however, were very similar because of higher Ca and Mg concentrations in drainage, especially in 1986 to 1988, from the red pine relative to the nonvegetated sandbox.

Bulk precipitation inputs **(precipitation).** Although the site received about 132 cm yr^{-1} of bulk precipitation during 1983 to 1988, Ca and Mg inputs averaged only 0.9 (Ca) and 0.3 (Mg) kg $ha^{-1}yr^{-1}$. Drainage losses of Ca and Mg were 13 to 39 times greater than precipitation inputs. Precipitation values include dust that settled in the funnel collector between rain events. Values do not include fine particles that may have impacted pine foliage in

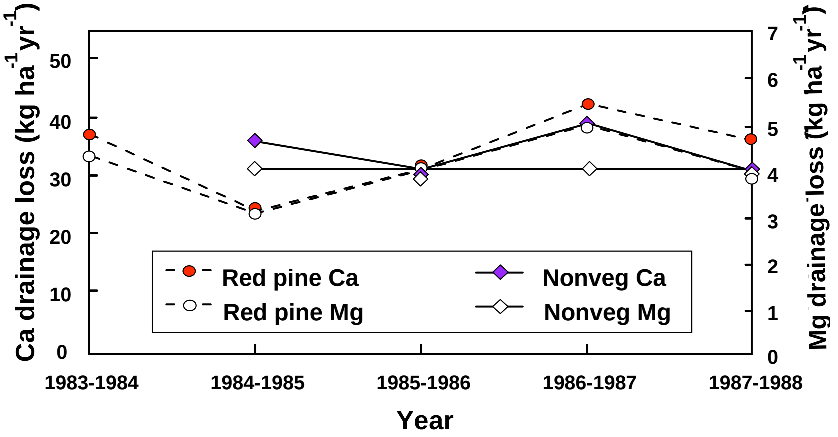

Figure 1. Similarity of annual drainage loss of Ca and Mg from red pine and nonvegetated sandboxes hides differences in concentration and water flux.

the sandboxes. If impaction occurred, weathering estimates would need to be adjusted downward. Pine sandboxes did have a 3- to 6-tree-wide buffer, and the White Mountain region is heavily forested with few areas of bare soil that could serve as sources of fine dust.

***Accumulation of Ca and Mg in plants and litter* (Δvegetation).** Biomass accumulated quickly in the pine sandbox, averaging about 15,000 kg ha^{-1} yr^{-1}, with about a third accumulating below ground (Bormann et al. 1993). Correspondingly, Ca and Mg in pine biomass and litter accumulated at 45 (Ca), and 3 (Mg) kg ha^{-1} yr^{-1}. This rate was similar to *drainage* for both Ca and Mg. Litter accumulated much slower than did living biomass, largely because of needle retention; red pine retains needles for 2 to 3 growing seasons. Thus, after the five growing seasons reported here, most of the needles produced were still held on the trees.

***Changes in products of weathering in soil* (Δproducts).** For the red pine sandbox, Ca and Mg accumulated even more rapidly in Δ*products* – averaging (with standard errors) 183 (91) and 85 (30) kg ha^{-1} yr^{-1}, respectively (Table 2). These rates are 3 (Ca) and 17 (Mg) times greater than Δ*vegetation* for red pine, making Δ*products* the largest component to the weathering equation. Rates were much lower and are not statistically significant for the nonvegetated sandbox, –9 (11) and 1 (6) for Ca and Mg, respectively. Concentrations of extracted Ca and Mg in soil products increased very rapidly in red pine sandboxes, especially at deeper depths, and changed little in nonvegetated soils (Figure 2). Red pine soil pools increase even though soil organic matter declined 20% (Bormann et al. 1993). Generally, extracted Ca

Table 2. Change in concentration and mass of extracted Ca and Mg (Δ*products*) for the red pine and nonvegetated sandboxes.

		Sampled soil depth zones (cm)					Calculated sum (cm)
	Units	0–10	10–20	20–30	30–80	80–130	0–130
Red pine sandbox							
Soil (<2 mm) mass	Mg ha^{-1}	1236	1215	1258	5992	6525	16224
Ca concentration							
1984§	g 10^{-6}g	419	431	‡399	‡406	‡402	
1988	g 10^{-6}g	352	388	400	453	489	
Ca mass							
Summed change	kg ha^{-1} 3.9 yr^{-1}	–83	–52	1	279	566	713
standard error		(33)	(23)	(50)	(223)	(285)	(355)
Annual rate of change	kg ha^{-1}yr^{-1}						183
standard error							(91)
Mg concentration							
1984§	g 10^{-6}g	103	98	‡97	‡94	‡98	
1988	g 10^{-6}g	110	109	110	117	121	
Change in Mg mass							
Summed change	kg ha^{-1} 3.9 yr^{-1}	9	14	16	140	152	330
standard error		(11)	(8)	(16)	(63)	(98)	(118)
Annual rate of change	kg ha^{-1} yr^{-1}						85
standard error							(30)
Nonvegetated sandbox							
Soil (<2 mm) mass	Mg ha^{-1}	1131	1104	1118	5515	6000	14868
Ca concentration							
1985§	g 10^{-6}g	348	398	399	406	ϕ402	
1993	g 10^{-6}g	305	385	393	405	402	
Change in Ca mass							
Summed change	kg ha^{-1} 7.8 yr^{-1}	–48	–15	–7	–4	0	–74
standard error		(26)	(24)	(31)	(70)	(ϕ)	(85)
Annual rate of change	kg ha^{-1} yr^{-1}						–9
							(11)
Mg concentration							
1985§	g 10^{-6}g	99	101	97	94	98	
1993	g 10^{-6}g	94	99	97	98	98	

Table 2. Continued.

	Units	Sampled soil depth zones (cm) 0–10	10–20	20–30	30–80	80–130	Calculated sum (cm) 0–130
Change in Mg mass							
Summed change	kg ha^{-1} 7.8 yr^{-1}	–5	–2	0	16	0	8
standard error		(8)	(10)	(8)	(45)	(0)	(48)
Annual rate of change	kg ha^{-1} yr^{-1}						1
standard error							(6)

Notes:
[‡] Samples in 1984 only go to 20 cm; 20–80 cm samples are assumed to be the same as those in the nonvegetated sandbox at the beginning of the experiment; original 80–130 cm values are from samples of the substrate before placement into the sandboxes; and initial 20–80 cm samples are not statistically different from initial sandbox substrate.
[ϕ] Samples only go to 70 cm; original 80–130 cm values are from samples of the substrate before placement into the sandboxes; and deeper soils are assumed to have changed little.
[§] Numbers include a depth adjustment factor: 1985: 30–80 cm = 30–70 cm$*$1.25.

increased with depth. In the nonvegetated sandbox, Ca and Mg concentrations in soil products declined slightly in the 0–10 cm depth and otherwise changed little from initial conditions. Substantial increases in concentrations of Ca and Mg were observed in the red pine sandbox throughout the profile for Mg and below 30 cm for Ca. Increasing Ca, and to a lesser extent Mg, concentration with depth may result from downward migration of original clay minerals contained in the tilled-in topsoil during the experiment and less root uptake.

Rates of primary mineral weathering

Estimates of the rate of primary mineral weathering differ sharply when the components are combined into equations 5–7 (Table 3), supporting our first hypothesis.

***Equation 5* (weathering = drainage – precipitation).** When Δ*vegetation* and Δ*products* are assumed to be in a steady state, the red pine sandbox had an estimated weathering rate of 33 (Ca) and 4 (Mg); the nonvegetated sandbox, had a rate of 34 (Ca) and 4 (Mg) kg ha^{-1} yr^{-1}. Considering the conservative estimates of standard errors, these rates are significantly greater than zero.

***Equation 6* (weathering = drainage – precipitation + Δvegetation).** When accumulation in red pine biomass is considered, estimates of the rate of

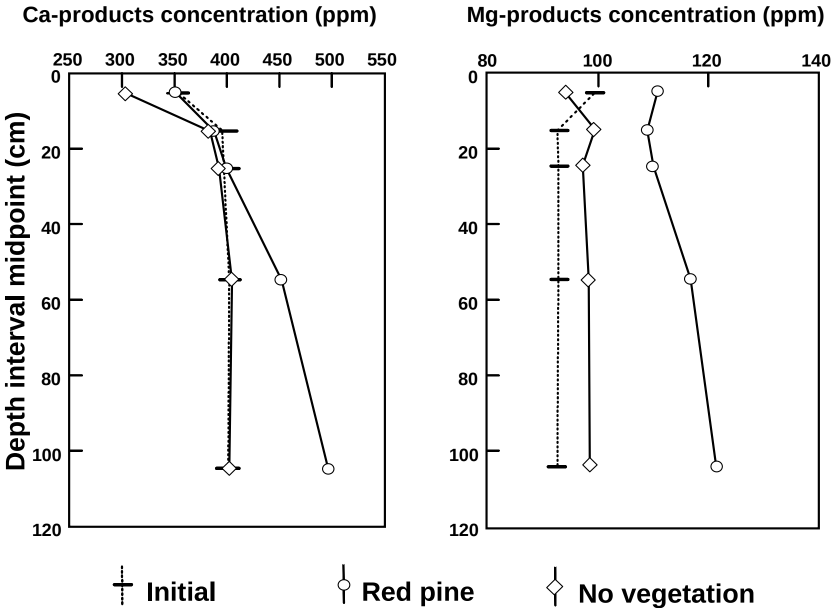

Figure 2. Concentration as a function of depth for nonprimary-mineral Ca and Mg (products of weathering in soil); initial conditions (nonvegetated sandbox only) and changes in red pine and nonvegetated sandboxes after 4 and 8 years, respectively.

weathering increased 2.4 (Ca) and 1.8 (Mg) times over equation 5 estimates to 78 (Ca) and 7 (Mg) kg ha^{-1} yr^{-1}. The lack of accumulation in vegetation in the nonvegetated sandbox results in no increase in estimated weathering (equation 6 compared to equation 5).

Equation 7 **(weathering = drainage – precipitation + Δvegetation + Δproducts).** When weathering is defined to contain the Δ*products* as well as the Δ*vegetation* terms, estimates of weathering increase sharply by 8 (Ca) and 23 (Mg) times to rates of 261 (Ca) and 92 (Mg) kg ha^{-1} yr^{-1}. Standard errors for these rates indicate they are statistically significant. These results support the first hypothesis – that the terms Δ*vegetation* and Δ*products* can be large and positive and, thus, that actual weathering can be more rapid than has been thought possible. Rapid weathering is explained mostly by large Δ*products* estimates for red pine (Table 2). The nonvegetated sandbox had a small, insignificant ($p < 0.05$) change in Δ*products* leading to an estimated weathering rate that is not statistically different from zero. Weathering rate estimates were 10 (Ca) and 18 (Mg) times higher in the pine sandbox relative to the nonvegetated sandbox estimate, when accumulation in vegetation and changes in soil products are included. The large vegetative accumulation and the dramatically higher rates of formation of the products of weathering

Table 3. Primary mineral weathering (kg ha^{-1} yr^{-1}) calculated as the sum of (*drainage – precipitation*) from eq. 5; +Δ*vegetation* from eq. 6; and +Δ*products* from eq. 7 for two sandbox ecosystems.

	Red pine				Nonvegetated			
Equation components and weathering estimates	Calcium		Magnesium		Calcium		Magnesium	
	kg ha^{-1} yr^{-1} (std. error)							
+*drainage*	34	(17)	4	(2)	35	(3)	4	(2)
–*precipitation*	1	(<1)	<1	(<1)	1	(<1)	<1	(<1)
+Δ*vegetation*	45	(7)	3	(<1)	0	(0)	0	(0)
+Δ*products*	183	(91)	85	(30)	–9	(11)	1	(6)
weathering (equation 5)	33	(17)	4	(2)	34	(3)	4	(2)
(equation 6)	78	(18)	7	(2)	34	(3)	4	(2)
(equation 7)	261	(93)	92	(30)	25	(14)	5	(6)

in soil in the pine versus nonvegetated sandbox results support the second hypothesis that weathering in ecosystems with vigorous plant growth is more rapid than in nonvegetated ecosystems.

Discussion

Weathering in aggrading ecosystems

Weathering rate estimates have mostly been based on watershed studies that assume vegetation and soils to be in a steady state, and thus rely on the difference between measured dissolved base elements in meteorological inputs and drainage losses (Table 4). Because this chemical denudation does not always reflect the actual weathering rate, the short-term significance of weathering for nutrient cycling has not been carefully examined. Two advances in technique allowed us to demonstrate the potential for large changes in soils on an ecosystem basis: the sandbox ecosystem method – by using fully homogenized soil inside a lined lysimeter – permitted quantitative estimates of drainage and soil changes over only a few years; and the analytical procedure developed by Rozan et al. (1997) extracted Ca and Mg associated with soil organic matter, amorphous residues, and various secondary minerals without significantly attacking primary minerals. These techniques offer a means of measuring ecosystem outputs, overcoming the high variability of natural forest soils, and – by adding buffer rows outside the

Table 4. Estimated rates of weathering release of Ca and Mg based on watershed mass-balance studies as compared to this study. Equation 5 assumes a steady state for soil and vegetation; equation 6 includes measures of Ca and Mg accumulation in vegetation.

			Weathering (equation 5) release of:		Weathering (equation 6) release of:		*Equation 6* Equation 5	
Location; (reference)	Parent material	Vegetation	Ca	Mg	Ca	Mg	Ca	Mg
				kg ha^{-1} yr^{-1}				
Pond Branch, MD; (Cleaves et al. 1974)	Serpentinite	Mixed hardwoods	trace	34	[§]—	—	—	—
Pond Branch, MD; (Cleaves et al. 1970)	Schist	Mixed hardwoods	1	2	—	—	—	—
Mont Lozere, France; (Lelong et al. 1990)	Monzonitic granite	Beech coppice	–1	2	3	2	—	1.5
Mont Lozere, France; (Lelong et al. 1990)	Monzonitic granite	Spruce forest	5	4	11	5	2.2	1.2
Mont Lozere, France; (Lelong et al. 1990)	Monzonitic granite	Grassland	5	2	7	3	1.4	
Luxenbourg; (Verstraten 1977)	Metashale	Mixed oak-beech	9	16	—	—	—	—
Hubbard Brook, NH; (Likens et al. 1977)	Granitic till	Northern hardwoods	11	2	21	3	1.9	1.4
Idaho batholith; (Clayton & Megahan 1986)	Quartz monzonite	Mixed-conifer	14	1	—	—	—	—
White Mountains, CA; (Marchand 1971)	Quartz monzonite	Sagebrush	17	2	—	—	—	—
Cascade Mountains, OR; (Fredriksen 1972)	Volcanic tuffs	Old-growth conifer	47	12	—	—	—	—
White Mountains, CA; (Marchand 1971)	Dolomite	Sagebrush	86	52	—	—	—	—
Hubbard Brook, NH; (sandbox study)	Granitic outwash	Non-vegetated	34	4	34	4	1.0	1.0
Hubbard Brook, NH; (sandbox study)	Granitic outwash	Red pine	33	4	78	7	2.4	1.8

[§] Change-in-vegetation data are not available in these studies.

lysimeters to form a uniform cover of young trees – reasonably extrapolating to a per-unit-area basis.

Under the conditions of our study, weathering supplies considerably more nutrients than would have been estimated by a chemical-denudation-based weathering estimate. When no change in vegetation and soil are assumed (equation 5), estimates of weathering rate in red pine sandboxes were 34 (Ca) and 4 (Mg) kg ha^{-1} yr^{-1}, close to the range of rates based on watershed studies, 1 to 17 (Ca) and 2 to 16 (Mg) kg ha^{-1} yr^{-1} (Table 4). Estimated rates for red pine increased by 2.4 (Ca) and 1.8 (Mg) times when accumulation in vegetation was considered. When both accumulation in vegetation and soils are considered, red pine rate estimates increased by close to an order of magnitude (8 times for Ca and 23 times for Mg) over rates with a steady-state assumption. Thus, when the small-watershed approach (Bormann & Likens 1979) is applied with steady-state assumptions for vegetation and soil, large underestimates of weathering rate are possible. This possibility is greatest in rapidly aggrading or degrading ecosystems where the assumptions of steady state are weakest, and suggests that more emphasis should be placed on understanding rates of mineral weathering in attempting to characterize nutrient cycles in both managed and natural systems, to improve the foundation for decisions about managing forested ecosystems sustainably.

Several lines of evidence support these conclusions. Bicarbonate can be a product of weathering (equation 1), and its discharge suggests weathering has occurred. Berner (1995) measured HCO_3^- in the sandbox effluent, normalized with Cl^- to correct for changes in all ions and in the reduced outflow resulting from evapotranspiration. Release of HCO_3^- in the red pine sandbox was large relative to the nonvegetated sandbox, especially during the growing season. Bicarbonate in drainage was estimated to be about 4 times greater in the red pine relative to the nonvegetated sandbox. This increase was not as large as the 10 (Ca) and 18 (Mg) fold increases from the nonvegetated to red pine sandbox estimates for equation 7, suggesting that weathering may be driven more by organic acids (equation 2) or that drainage is affected by other sources and sinks of bicarbonate, such as uptake of base elements in plants and decomposition.

Biotic enhancement of weathering in the red pine sandbox was also suggested by the increase in the ratio of sodium to chloride in drainage waters from the sandboxes. From November 1984 to July 1990, drainage waters from 44 dates were also analyzed for chloride (Berner 1995). The volume-weighted average concentrations of Na and Cl expressed as a Na:Cl ratio were 5.5 for the nonvegetated and 14.5 for the red pine sandbox. Chloride is not an important plant nutrient nor a constituent of primary minerals found in the sandbox soils, and thus can be considered a conservative tracer of precipitation flux through the sandboxes over the almost 6-yr period. Sodium flux out of the boxes can be enhanced via weathering of the minerals found in the sandbox substrate. This flux is not greatly affected by vegetation uptake because sodium is not a plant nutrient. The measured ratio of Na:Cl in precipitation is about 0.7 (Buso, pers.comm.), and thus the enhancement in the nonvegetated box suggests some weathering of fresh mineral surfaces during the experiment. The more than 2-fold higher Na:Cl ratio in the red pine relative to the nonvegetated sandbox is consistent with the results from equation 6, which indicated a 2-fold increase in weathering of Ca and Mg in the red pine relative to the nonvegetated sandbox. Sodium flux in drainage waters would not reflect the components of weathering expressed in equation 7.

With detailed mineralogical and chemical information, chemical reactions that closely approached those in the soil can be written (Table 1), and their approximate order of importance given, based on estimates of weathering in acidic soil environments (Pettijohn 1941; Goldich 1968). The reactions in Table 1 assume congruent dissolution and release to the soil solution. Although biotite, for example, was at least partially transformed incongruently to vermiculite, based on x-ray diffraction, energy dispersive spectrometry, electron microprobe, and scanning electron microscopy, incongruency should have little influence on the release of most of the base elements into solution. Scanning electron microscopy of feldspars, hornblende, pyroxene, garnet, epidote, and apatite; however, showed no significant amounts of newly formed secondary minerals developing on the surfaces of mineral grains. This finding is consistent with other studies in the laboratory and in the field (e.g., Holdren 1979; Velbel 1988; Berner & Schott 1992). Therefore, we concluded that most of these reactions are likely in the sandbox soils and that dissolution of these minerals could have released considerable amounts of Ca and Mg to the soil solution. The abundance of minerals in the sandboxes (Table 1), together with estimates of their relative weathering rates, suggested that biotite and hornblende were the primary sources of Mg, and plagioclase and hornblende were the primary sources of Ca.

Weathering contributions to plant-available pools

The potential for rapid plant-induced weathering in soils raises important questions about concepts of nutrient availability. Cations in soil solution and on exchange sites have not been effective measures of the long-term (one year or longer) capacity of a soil to supply base-element nutrients because, for example, rapid uptake from decomposing organic matter is not well reflected, and episodic root and microbe uptake can influence concentrations independent of supply. Long-term plant uptake of nutrients offers a seemingly direct measure of availability; because plants can vary in their ability to acquire

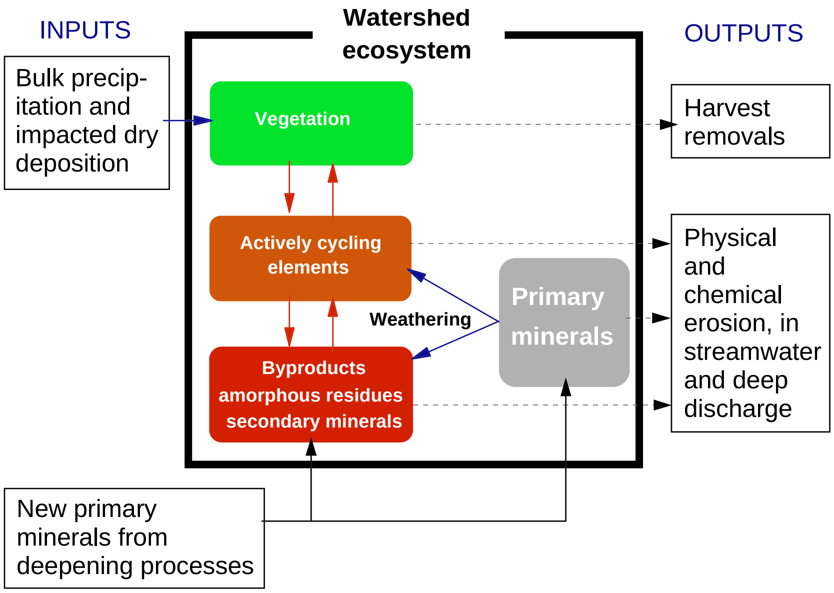

Figure 3. An ecosystems perspective on weathering and long-term base-element availability. Weathering appears to transfer base elements to either available or nonavailable pools of soil products. If the nonavailable pool becomes large relative to the primary mineral pool (e.g., flat tropical soils) then soil deepening and erosion become key processes to increase base-element availability.

nutrients, estimates of availability may depend on which species are present. Different assemblages of organisms also have a large effect on the potential nutrient supply. They directly or indirectly influence weathering reactions (Quideau et al. 1996) by releasing organic acids, mostly by mycorrhizal fungi (Jongmans et al. 1997); by changing soil acidity, atmosphere, and hydrology; by their rooting strategies; and by facilitating disturbances like windthrow (by growing tall enough to be uprooted). Using ion-exchange resins to estimate availability may avoid organism- or assemblage-based inconsistencies, but does not simulate active uptake processes and also does not account for diffusion rates (Abrams & Jarrell 1992). In our study, weathering release of Ca and Mg actually exceeded plant uptake. Much of the plant uptake we observed must have come from weathering reactions of primary minerals, rather than from the soil-products pool because – although some Ca and Mg may have come from the *products* pool – it is a net sink. Thus, the weatherability of primary minerals can influence availability of base-element nutrients.

An alternative approach to defining base-element availability for a given soil, therefore, would be to evaluate all of the primary-mineral and soil-products pools (Figure 3) to determine the potential availability of elements to effective plant-microbe associations. Included in this analysis would be estimates of the weatherability of primary minerals based on known factors such as mineral composition, particle-size and total surface area, coatings that reduce effective surface area, rooting depth, and climate. The interpretation of Δ*products* has indirect implications for ecosystem productivity as well. Accumulation of *products* may involve both increases and decreases in base-element availability by formation of soil organic matter, amorphous residues, and other secondary minerals. Weathering reactions may involve solution phases where Ca and Mg are readily available, but they also result in thermodynamically more stable products. Accumulation of poorly available or unavailable Ca and Mg in *products* can, however, indirectly affect productivity by increasing cation-exchange surfaces and water-holding capacity. A long-term bioavailability index based on these factors might provide new insights into the role of base elements in sustaining plant growth.

Weathering in ecosystems

Weathering of primary minerals is a feature internal to the ecosystem (Bormann & Likens 1967, 1979). Over time, a gradient of primary minerals develops where fewer primary minerals are found near the soil surface where weathering has been most intense (van Hise 1904; Lutz & Chandler 1946). Given sufficient time in some soils – like tropical Oxisols – deep accumulation of inert secondary minerals will limit access of roots to nutrients from weathering. Similarly, till soils of southeast Alaska can rapidly develop dense spodic horizons that limit rooting to organic and upper mineral soil horizons (Bormann et al. 1995). Thus, changes in nutrient cycling and sustainability can be better understood when mechanisms to resupply the ecosystem with weatherable primary-mineral substrate are considered (Figure 3). Mechanisms to resupply primary minerals have different time frames. Among the processes that move primary minerals from a deeper position to the zone of more intense weathering near the surface are animal burrowing with a time frame of decades (Cox 1984); upturned rootwads from windthrow with a time frame of centuries (Lutz 1940; Bormann et al. 1995); landslides with a longer time frame (Scatena 1995); and ultimately glaciers and volcanic eruptions. A primary mechanism for the downward extension of the ecosystem boundary is through root exploration, sometimes to surprising depths of 10 m or more (Nepstad et al. 1994) and more than 3 m into fractured bedrock in cracks as narrow as 100 μm (Zwieniecki & Newton 1994). In effect, higher plants move sources of hydrogen ion (CO_2, detritus, and organic acids) in close proximity to weatherable primary-mineral surfaces.

Weathering and ecosystem sustainability

The possibility that weathering plays a significant role in the release of nutrients available to plants has to be rescued from generally accepted slow rates derived from watershed studies based on steady-state assumptions. We demonstrate the potential for rates that are about ten times faster, at least under conditions where primary minerals are abundant, soils have been disturbed, and plants are growing rapidly. Faster rates like this become extremely important where managers are trying to maintain nutrients available to plants by balancing precipitation and weathering release with outputs including harvest removals.

Clearly, a wealth of research questions need to be addressed as we seek to redefine weathering as a significant short-term process. Questions to be addressed include Do species differ in their capacity to induce rapid weathering? Do processes that mix soil layers control base-element supply through effects on rate of weathering? What is the role of erosion in maintaining weathering rates? How does weathering change in time and space with disturbance and plant succession? What effects does rapid weathering have on physical properties of soil important to productivity? What role do amorphous residues have on nutrient availability?

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