

Changing sources of base cations during ecosystem development, Hawaiian Islands

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ABSTRACT

⁸⁷Sr/⁸⁶Sr evidence from a soil chronosequence in the Hawaiian Islands demonstrates that the atmosphere supplies >85% of putatively rock-derived Sr in older sites. Initially, bedrock is the dominant source for Sr and other lithophile elements such as Ca, but high rates of weathering and leaching of the substrate by 20 ka lead to a shift to atmospheric sources. The loss of weathering inputs coincides with other physio-chemical changes in the soil and results in a steep decline of base cations in the soil pool. While these patterns imply the potential for limitation of biological productivity by low base cation supply, the atmosphere provides a supply of base cations in excess of nutritional needs, even after nearly all rock-derived base cations have been leached from the soil. This raises the possibility that P limitation in terrestrial ecosystems may develop at least as much because of low rates of atmospheric deposition of P (relative to Ca, K, and other rock-derived elements) as because of its chemical interaction in soil.

INTRODUCTION

There is a fundamental distinction between biogeochemical cycles of atmospheric versus lithospheric affinity; they are regulated differently and have differing effects on biological systems (Walker and Syers, 1976). Nutrient elements commonly believed to originate from lithospheric sources include P, K, Ca, and Mg (Schlesinger, 1997). Recent challenges to this paradigm are suggested by (1) studies identifying the atmosphere as a potentially important source of base cations in soil-plant systems (Dahms, 1993; Hedin and Likens, 1996; Hedin et al., 1994; Zarin and Johnson, 1995); (2) data indicating that base cations can be leached from soils faster than they are supplied by weathering in mineral-acid impacted soils (Likens et al., 1996; Schultze, 1989); and (3) Sr isotopic studies that suggest that atmospheric sources of Sr dominate in some ecosystems (Capo et al., 1998; Miller et al., 1993; Åberg et al., 1989; Gosz and Moore, 1989; Graustein and Armstrong, 1983). Atmospheric dominance of putatively weathering derived elements has important implications for our understanding of (1) nutrient cycling (Walker and Syers, 1976); (2) the long-term ability of soil to buffer natural and anthropogenic acidification (Reuss et al., 1987); and (3) Ca and Mg deficiencies in some tree species in polluted northern temperate forests and in highly weathered soils (Federer et al., 1989).

Here we report ⁸⁷Sr/⁸⁶Sr and elemental data from plants and soils along a chronosequence in Hawaii. We use this well-studied and tightly constrained system (Vitousek et al., 1997) to isolate

the influence of changing substrate age and hence the weathering input. Whereas changes in substrate composition and nutrient supplying capacity have previously been modeled, assumed, or inferred from point measurements in other systems (e.g., Zarin and Johnson, 1995; Miller et al., 1993; Graustein and Armstrong, 1983), the Hawaiian chronosequence is well-enough constrained to allow quantitative evaluation of the developmental shift from weathering to atmospheric sources of Sr as soils and ecosystems age. We demonstrate that, by varying substrate age (and weathering state), a range of atmospheric contribution of Sr from <5% to >90% is possible in otherwise similar systems.

Sr ISOTOPES AS TRACERS IN ECOSYSTEMS

Base cation cycles in forested ecosystems are difficult to study because the flux of bedrock weathering products to forest soils cannot be measured directly. The isotopes of Sr are useful tools for studying the provenance of base cations because ⁸⁷Sr/⁸⁶Sr ratios in atmospheric and bedrock weathering sources often differ, providing a tracer of sources of Sr within the plant-soil-hydrological system (Capo et al., 1998; Bailey et al., 1996; Miller et al., 1993; Åberg et al., 1989; Graustein, 1989). Natural variations in the isotopic composition of Sr reflect solely the difference in source contributions, because any potential fractionations (biological or analytical) are removed by normalization to a constant ⁸⁶Sr/⁸⁸Sr (Faure, 1986). Sr is chemically similar to Ca (Romney et al., 1957) and provides a useful proxy for this essential nutrient. Other important lithophile elements such as Mg, K, and P are subject to different chemistry within the soil than

Sr. However, useful qualitative information on the cycles of these elements can be derived using Sr isotopes because their ultimate sources are similar to those of Sr.

The relative contribution of Sr from weathering and atmospheric sources can be determined in plant, soil, or water samples using a weighted mixing equation where X_{atm} represents the mass fraction of Sr derived from the atmospheric source and $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{atm}}$ and $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{wea}}$ refer to the atmospheric and weathering source end member, respectively:

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{sample}} = X_{\text{atm}} \times \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{atm}} + (1 - X_{\text{atm}}) \times \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{wea}} \quad (1)$$

The usefulness of this technique depends on accurate identification of the Sr isotopic composition of both rock and atmospheric sources; rarely a simple task for either end member. The heterogeneous mineral assemblages that compose bedrock typically have different ⁸⁷Sr/⁸⁶Sr ratios and weather at different rates. Consequently, as rocks weather, the ⁸⁷Sr/⁸⁶Sr value of soil solution and remaining minerals differ from the original whole rock value (Bailey et al., 1996; Blum and Erel, 1995). The atmospheric contribution consists of dissolved cations in rain water and dust fall; the latter is especially significant in dry continental interiors (Dahms, 1993; Hedin et al., 1994; Graustein and Armstrong, 1983). Dissolved ions in precipitation are immediately available for plant uptake, whereas dust minerals and bedrock minerals must be weathered prior to release of Sr. The ⁸⁷Sr/⁸⁶Sr value for precipitation and dust can vary temporally as well as spatially (Bailey et al., 1996; Gosz and Moore, 1989). Despite recognition of large dust contributions to the Sr budget of soil (Graustein and Armstrong, 1983), no studies have attempted to separate the influence of incongruent weathering of the dust fraction from the dissolved-ion atmospheric end member.

The Hawaiian chronosequence is ideally suited to study changes of base cation sources as a function of substrate age because it minimizes the influence of factors other than substrate age and maximizes the accuracy with which Sr isotopic

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end members can be assigned. Sites are located on minimally eroded constructional surfaces with virtually identical initial geochemical composition, rainfall (250 cm), temperature (16 °C), and species composition (dominant species in all sites is *Metrosideros polymorpha*) (Vitousek et al., 1997; Crews et al., 1995). The rock weathering end member is the same as the whole rock $^{87}\text{Sr}/^{86}\text{Sr}$ because the young age and low Rb/Sr has minimized isotopic differentiation by mineral species (Capo et al., 1998). The dissolved-ion atmospheric end member is dominated by sea-salt aerosols that have constant marine $^{87}\text{Sr}/^{86}\text{Sr}$ values, but it is augmented by radiogenic dust derived from Asia (Nakai et al., 1993). An integrated estimate of dust input can be derived from measurement of the quartz in soils because quartz is not a component of the underlying mantle-derived basaltic lava (Jackson et al., 1971).

Sr ISOTOPIC VALUES

Soils and tree leaves (*Metrosideros polymorpha*) were sampled and analyzed for $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr elemental concentration from six sites on basalt substrates ranging in age from 0.3 ka to 4100 ka (Table 1). The exchangeable component of Sr and Ca in soil samples was extracted using 1 M ammonium acetate (Carter, 1993), and the extract was digested in ultrapure $\text{HClO}_4 + \text{HNO}_3$.

Leaf-tissue samples were ashed at 550 °C, and the residue was digested in ultrapure HClO_4 and HNO_3 . Sr from the soil and leaf digests was separated for isotopic analysis using Eichrom Sr Specific Resin. Analytical uncertainties based on repeat analysis of standards for isotopic analysis are ± 0.000009 (NBS-987 averaged 0.710246), and for concentration data they are $\pm 5\%$.

Sr isotopic data from soils and plants on the Hawaiian chronosequence demonstrate a pronounced shift in sources of Sr with time. Ecosystem Sr is derived from rock weathering in the 0.3 and 2 ka sites, from a mixture of atmospheric and weathering sources by 20 ka and from atmospheric inputs in sites 150 ka and older (Figs. 1 and 2). The shift from bedrock to atmospheric source is driven by intense leaching of Sr from the substrate that is offset by a continuous but dilute atmospheric flux. Comparison of nutrient element/immobile element ratios within the soil to similar ratios in the original basalt substrate provides independent confirmation that lava weathering delivers a relatively short-term supply of ecosystem nutrients (Chadwick et al., 1994). After 20 k.y., less than 1% of the Sr and Ca from the primary minerals remains in the soil (Fig. 3); K, Mg, and Si are also strongly depleted (Vitousek et al., 1997). The Ca and Sr retained on the soil-exchange complex that is readily available to

plants is also depleted (Fig. 3) because natural physiochemical processes (including acidification, Al and Fe residual enrichment, and the loss of highly adsorptive minerals) reduce base cation retention capacity (Torn et al., 1997). The combined effect is a substantially depleted nutrient pool and a dominance of atmospheric sources of base cations in rainforests growing on all but the youngest Hawaiian volcanoes.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of plant leaves reflect the soil values (Fig. 2), demonstrating a close relationship between Sr in the soil exchange pool and that taken up by plants. An apparent contradiction to this relationship occurs at the 20 ka site where the depth-weighted average soil $^{87}\text{Sr}/^{86}\text{Sr}$ is considerably more radiogenic than the plant values. In this case, the depth-weighting procedure masks a stratigraphic change in age of parent material. The sharp $^{87}\text{Sr}/^{86}\text{Sr}$ increase at 30 cm depth (Fig. 1) coincides with an abrupt transition in soil morphology that separates a recent, thin Mauna Kea ash fall from an earlier thicker ash deposit. Plant values reflect the $^{87}\text{Sr}/^{86}\text{Sr}$ of the upper horizon. The isotopic shift recorded in Figure 1 confirms soil stratigraphic observations, indicating that the lower horizons are more strongly weathered than the upper ones. The parallel features in the soil exchange $^{87}\text{Sr}/^{86}\text{Sr}$ and soil stratigraphy demonstrate that Sr isotopes can reflect base cation sources in soils with high resolution, and that Sr isotopes in plant material can be a sensitive indicator of the depth in the soil column at which plants obtain base cations.

TABLE 1. SUMMARY OF ISOTOPIC DATA AND RESIDENCE TIME FOR THE LONG SUBSTRATE AGE GRADIENT

Site	Age (ka)	DWM soil ($^{87}\text{Sr}/^{86}\text{Sr}$)	Atm (%)	Avg. leaf ($^{87}\text{Sr}/^{86}\text{Sr}$)	Ca residence time: years	
					Soil exchange	Total
Thurston	0.3	0.7041	10	0.7043	10	-
Ola'a	2	0.7040	5	0.7039	19	-
Laupahoehoe	20	0.7080	75	0.7056	8	23
Kohala	150	0.7089	90	0.7078	5	69
Molokai	1400	0.7088	89	0.7088	9	46
Kauai	4100	0.7085	84	0.7085	22	186

Note: DWM is the depth weighted mean $^{87}\text{Sr}/^{86}\text{Sr}$ in the soil exchangeable $^{87}\text{Sr}/^{86}\text{Sr}$ leaf of the average of *Metrosideros polymorpha* leaves (average standard deviation on 12 replicate samples from trees at the study sites = 0.000041); % Atm. corrected for radiogenic dust contribution by using 0.7 end member. The residence time for the total Ca pool in the younger sites is not reported if primary mineral Ca that is not available on the time scale of interest (10-100 yr). In the case of Kauai, which has exhausted Ca in the substrate (see Fig. 3), total Ca in the soil reflects the exchangeable Ca.

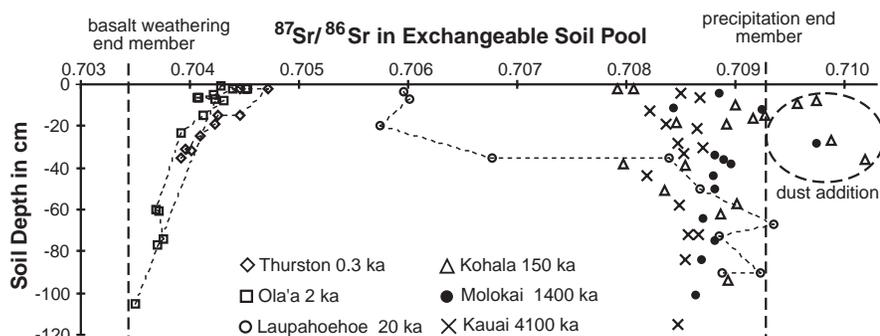


Figure 1. $^{87}\text{Sr}/^{86}\text{Sr}$ of exchangeable (1 M NH_4Ac) component of soil plotted against soil depth (cm). At each site, five to seven horizons were analyzed in replicate two to four times (for a total of 53 measurements). Maximum standard deviation (s.d.) among replicates was 0.00105 and average s.d. = 0.00025, indicating high degree of homogeneity of isotopic composition within given soil horizon.

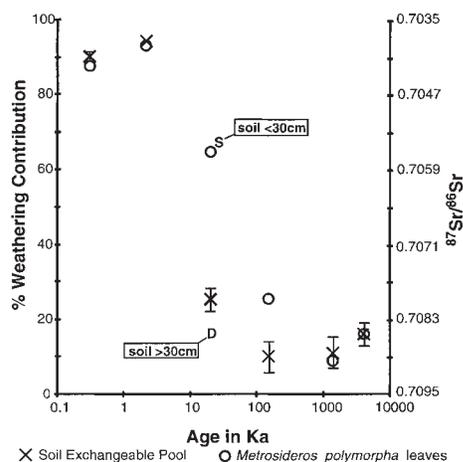


Figure 2. Weathering contribution (%) to depth weighted mean of $^{87}\text{Sr}/^{86}\text{Sr}$ within exchangeable soil pool for each site and for *Metrosideros polymorpha* leaves, plotted against age in thousands of years. Weathering percentage in soil and plant values is calculated using dust-corrected atmospheric end member of 0.7095 (this includes 3% dust contribution with $^{87}\text{Sr}/^{86}\text{Sr}$ release of 0.718). Error bars indicate range of possible values using no dust correction to maximum values for dust flux and isotopic composition reported in Nakai et al. (1993). Additional values provided for 20 ka site correspond to upper soil (S) and lower soil horizon (D) discussed in text.

In light of the rapid and intense depletion of lithophile nutrients, it is surprising that weathering appears to contribute 10%–20% of the plant and soil Sr in the oldest sites, even to 4100 ka. Maintenance of some weathering-derived Sr could be explained by (1) mining of the saprolite-bedrock interface by tree roots or (2) locally derived basalt dust from canyons and beaches. We see no other sources that could provide $^{87}\text{Sr}/^{86}\text{Sr}$ at sufficiently low ratios. The former explanation is mildly unsettling, however, because the bedrock-saprolite interface is overlain by more than 10 m of nutrient-deficient and Al-enriched saprolite at this oldest site. The second possible explanation would require a relatively large amount of locally derived dust deposition ranging from $60 \mu\text{g}$ to $223 \mu\text{g cm}^{-2} \text{yr}^{-1}$ of basalt dust, assuming $\sim 300 \text{ ppm}$ Sr in tholeiitic basalt (Feigenson et al., 1983).

INFLUENCE OF ASIAN DUST ON THE ATMOSPHERIC END MEMBER

At the 150 and 1400 ka sites, some $^{87}\text{Sr}/^{86}\text{Sr}$ soil values are significantly higher than the sea-salt end member (0.7092) (Fig. 1). These horizons also contain quartz and mica that are deposited as mineral aerosol (tropospheric dust) blown from Asia (Jackson et al., 1971; Dymond et al., 1974). North Pacific deep-sea-core data indicate that this dust has significantly higher $^{87}\text{Sr}/^{86}\text{Sr}$ (0.715 to 0.721) than sea-salt aerosols (Nakai et al., 1993). We estimate its influence on the $^{87}\text{Sr}/^{86}\text{Sr}$ of the atmospheric end member as follows. Assuming a long-term rainfall input of $\sim 250 \text{ cm yr}^{-1}$, and dissolved Sr of $\sim 1 \text{ ng g}^{-1}$, provides a marine-derived Sr flux of $250 \text{ ng cm}^{-2} \text{yr}^{-1}$ to the soils. Fixing dust-flux values at $1 \times 10^{-5} \text{ g cm}^{-2} \text{yr}^{-1}$ for interglacial times and $4 \times 10^{-5} \text{ g cm}^{-2} \text{yr}^{-1}$ for glacial times (Rea, 1994) provides a deposition rate of Sr of $2 \text{ ng cm}^{-2} \text{yr}^{-1}$ (interglacial) to $8 \text{ ng cm}^{-2} \text{yr}^{-1}$ (glacial), assuming a 200 ppm Sr concentration (Nakai et al., 1993). These values are open-ocean dust fluxes representing a minimum estimate of dust deposi-

tion. Dust input is positively correlated with precipitation, which in these sites is enhanced three fold relative to the open ocean by the orographic effects of the islands (Gavenda, 1992). Correcting the atmospheric end member by using this range in dust flux and isotopic values introduces a 1%–6% uncertainty in our calculation of the weathering-derived Sr fraction (Fig. 2).

As an additional means to estimate the maximum influence of dust weathering on the $^{87}\text{Sr}/^{86}\text{Sr}$ of the exchange pool of Sr, we utilized a correlation between quartz (used as a proxy for dust) and $^{87}\text{Sr}/^{86}\text{Sr}$ of the exchangeable soil pool at the dustiest site (150 ka). Using the zero-quartz intercept value (0.7082) and a dust-free atmospheric (sea salt) end member of 0.7092, we calculate a rock-weathering contribution of 18% (compared to the 10% rock weathering contribution calculated using the dust correction applied in Fig. 2). Using the difference between the $^{87}\text{Sr}/^{86}\text{Sr}$ depth-weighted mean of the soil pool and the “dust-free” intercept (0.7082), and an estimate of the isotopic ratio of Sr released from dust, we find that dust weathering contributes 5%–18% of the exchangeable Sr pool at this site (Fig. 4). Even in the remote Hawaiian archipelago, an external dust source provides a significant portion of the total Sr budget. In most continental areas, these contributions will be much higher, requiring careful characterization of this end member.

IMPLICATIONS FOR ECOSYSTEM NUTRIENT DYNAMICS

Our Sr isotopic results provide clear evidence that the dissolved ion component of atmospheric input becomes the dominant source of Sr to developing Hawaiian ecosystems. This is true for some of the major lithophile nutrients as well. The amount of Ca contributed from each end member can be calculated from the Sr isotopic ratio if the Sr/Ca ratio is known for each end member. In general, Sr is a good proxy for Ca and largely follows similar trends of deple-

tion (Fig. 3), but a significant divergence in the chemistry of these elements is evident in the rising Sr/Ca ratio within different soil pools and plants across the chronosequence. This trend contrasts with an expected decline if Ca were concentrated by biocycling processes (Elias et al., 1982). The most rapid rise in the Sr/Ca ratio occurs within the remaining mineral phases (total Sr pool), suggesting a fractionally higher rate of Ca leaching relative to Sr (Fig. 3). The initial rise within the exchangeable soil pool and plants is likely related to mixing with the atmospheric source ($\text{Sr}/\text{Ca} \approx 0.018$) relative to weathering tholeiitic basalt ($\text{Sr}/\text{Ca} \approx 0.006$). Past 20 ka, however, the Sr/Ca ratio of the total soil pool rises and exceeds the atmospheric end member, almost reaching unity in the 4100 ka site. In this system, we can ignore the difference in Sr/Ca ratios in the 20 ka and older sites because the ratio of the total pool exceeds that of the atmospheric end member. In sites where weathering contribution of Sr is in excess of Ca relative to the atmospheric source, the minimal weathering contribution determined from the Sr isotopic ratio can be treated as a conservative estimate.

Using $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to constrain weathering contributions to the soil, we calculate the residence time of exchangeable Ca and total Ca in the soil of older sites ($>20 \text{ ka}$) to be on the order of decades and centuries, respectively. Residence time in the exchangeable pool of Ca is deter-

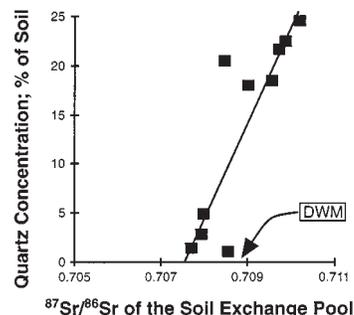
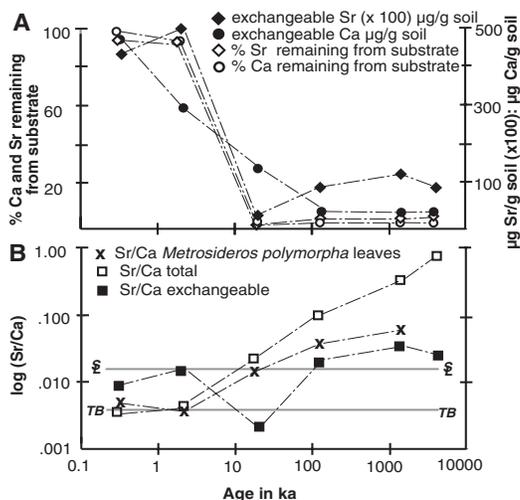


Figure 4. Quartz concentration in soil plotted against $^{87}\text{Sr}/^{86}\text{Sr}$ of exchangeable pool for 150 ka site. We use empirical relationship between soil quartz content ($R^2 = 0.68$; $n = 10$), and $^{87}\text{Sr}/^{86}\text{Sr}$ within soil exchangeable pool to estimate $^{87}\text{Sr}/^{86}\text{Sr}$ of Sr release from dust weathering. Dust contribution of Sr to exchange pool can be estimated from difference between 0% quartz intercept value = $(^{87}\text{Sr}/^{86}\text{Sr})_0$ and depth weighted mean of $^{87}\text{Sr}/^{86}\text{Sr}$ in soil = $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{DWM}}$:

$$X_{\text{dust}} \times \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_{\text{dust}} = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_{\text{DWM}} - \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_0$$

We estimate $^{87}\text{Sr}/^{86}\text{Sr}$ of dust component as 0.717 ± 0.005 , allowing for possibility of temporal variability or selective dissolution of dust minerals. Quartz intercept of 0% is ~ 0.7082 , yielding range of 5% to 18% dust-derived Sr for soil-exchange pool depending on $^{87}\text{Sr}/^{86}\text{Sr}$ value assigned to weathering release (0.722 to 0.712).

Figure 3. A: Percent loss of Ca and Sr from substrate against time, calculated by comparing ratio of Ca and Sr and immobile elements (Zr and Ti) with those in original basalt substrate (Vitousek et al., 1997). Exchangeable (1 M NH_4Ac) Ca and Sr concentration within the soil. B: Sr/Ca elemental ratios for the exchangeable soil pool, total acid-digested soil pool, *Metrosideros polymorpha* leaves (average value of two replicates), and end members. TB—tholeiitic basalt (Feigenson et al., 1983); S—sea water; L—Nanking Loess (Taylor et al., 1983).



mined by dividing the total soil pool and above-ground Ca in biomass (calculated from Vitousek et al., 1995, 1997; Herbert, 1995) by the sum of atmospheric deposition and weathering contributions. In sites older than 20 ka, the small weathering contribution (<15%) coupled with the higher Sr/Ca ratio in the weathering substrate means that Ca from weathering provides a minimal addition to the atmospheric flux and can be ignored in older sites. Although precipitation Ca concentrations are highly variable (0.12–2.64 mg L⁻¹), we utilize a value (0.41 mg L⁻¹ for combined wet and dry) obtained from an altitude similar to our sites, and note that other values within the reported range would not greatly change the conclusions here (Ericksson, 1957). The basalt weathering flux is the fraction of the atmospheric contribution determined from the ⁸⁷Sr/⁸⁶Sr of the exchangeable soil pool and reported in Table 1.

The short residence time for Ca indicates that the atmospheric flux is likely to be adequate to meet ecosystem requirements despite the decline of the soil-nutrient pool, a result that is also likely to be true for other important base cations such as K and Mg. It is not likely to be true for P, however. While P undergoes depletion from primary minerals, it becomes progressively immobilized in soils (Walker and Syers, 1976; Vitousek et al., 1997), and is replenished from atmospheric supply at least 100 times more slowly than Ca. Consequently, P has a residence time that is two to three orders of magnitude longer than Ca.

Fertilization experiments with P and base cations demonstrate that P is the limiting macronutrient at the older chronosequence sites, and additions of base cations have no effect on plant growth (Vitousek and Farrington, 1997; Herbert and Fownes, 1995). Together these results show that, in spite of a dramatic decline in the supply of Ca, Mg, and K, the base cation supply in these sites is robust over the long term. Initial rainforest aggradation is satisfied by a flush of lava-derived base cations, and later forest productivity is sustained by more dilute atmospheric sources.

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