

Uplift, Erosion, and Phosphorus Limitation in Terrestrial Ecosystems

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ABSTRACT

Primary productivity on old, weathered soils often is assumed to be limited by phosphorus (P), especially in the lowland tropics where climatic conditions promote the rapid depletion of rock-derived nutrients. This assumption is based on a static view of soils weathering in place with no renewal of the bedrock source. In reality, advection of material through the soil column introduces a spatially variable supply of rock-derived nutrients. This flux is dependent on the residence time of soil, which can range from a few hundred years in rapidly uplifting collisional mountain belts to tens of millions of years in tectonically quiescent tropical cratons. We modeled the effects of tectonic uplift, erosion, and soil depth on the advection of P through the soil column and P availability, calibrating rate of change in biologically available P over time with data from two basaltic chronosequences in Hawai'i and a series of greywacke terraces in New Zealand. Combining our model with

the global distribution of tectonic uplift rates and soil depths, we identified tectonic settings that are likely to support P-depleted ecosystems—assuming that tectonic uplift and erosion are balanced (that is, landscape development has reached steady state). The model captures the occurrence of transient P limitation in rapidly uplifting young ecosystems where mineral weathering is outpaced by physical erosion—a likely occurrence where biological N fixation is important. However, we calculate that P depletion is unlikely in areas of moderate uplift, such as most of Central America and Southeast Asia, due to the continuous advection of P into the rooting zone. Finally, where soil advection is slow, such as the Amazon Basin, we expect widespread P depletion in the absence of exogenous nutrient inputs.

Key words: uplift; erosion; nutrients; phosphorus; soil age; limitation.

INTRODUCTION

Nutrient limitation to primary productivity is widespread in both terrestrial and oceanic ecosystems, and may constrain the biological responses to global changes such as rising greenhouse gas concentrations (Nadelhoffer and others 1999; Shaw and others 2002). Productivity on young soils often

is limited by nitrogen (N), which is virtually absent from most rocks (Vitousek and Howarth 1991) although transient phosphorus (P) co-limitation can occur in young soils where mineral P has not had time to dissolve into biologically available forms (Chapin and others 1994). In contrast, ecosystems on old substrates are thought to be limited primarily by phosphorus (P), which is initially made available by mineral dissolution but is subsequently lost or otherwise rendered unavailable to plants as soils age (Walker and Syers 1976; Vitousek 2004; Wardle and others 2004). P limitation may be

Received 20 March 2006; accepted 9 August 2006; published online 28 February 2007.

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particularly pronounced in lowland tropical rain forests; the absence of glaciation there means that many soils are older than most temperate soils, and the warm wet climate causes relatively rapid depletion of rock-derived P (Tanner and others 1998). Studies of chronosequences (sites that vary in age but are relatively constant in the other factors that control soil properties) confirm that P availability initially increases, and then gradually declines as soils age (Wardle and others 2004).

The classical view that soils start with an initial amount of mineral P that is not replenished by additional bedrock inputs (Walker and Syers 1976) assumes static geomorphic surfaces. In actuality, surface erosion, the downward propagation of the soil/bedrock interface, and tectonic uplift, continually advect fresh material to the bottom of the soil column (Hilley and others 2006). In some sites advection can provide a substantial input of rock-derived nutrients to ecosystems (Bern and others 2005).

Here we present a framework to explore where the supply of rock-derived P to ecosystems by advection is insufficient to keep pace with P loss and occlusion into biologically unavailable forms—the necessary condition for generating long-term P depletion. In our formulation, soil particles enter the bottom of the soil column and are eventually eroded from the surface. Their residence time in soil (τ) is the ratio of the soil thickness (Z_s) to the erosion rate (ϵ). We postulate that the same increase and decay of available P observed across chronosequences occur in the soil column: as a rock fragment is incorporated into the soil, apatite dissolves, and then available P is gradually lost from the biologically available pool. Concurrently, the downward propagation of the soil column results in higher concentrations of mineral P at the bedrock/soil interface, and the loss and/or occlusion of P toward the soil surface—such that a soil may be viewed as an age gradient running from bottom (young) to top (old) (Figure 1). Qualitatively, P limitation is most likely either where erosion removes soil particles before mineral P has time to dissolve (short soil residence times) or where available P has been lost or occluded before much of it reaches the rooting zone in the upper part of the soil profile (very long soil residence times). These are regions with thin soils and high erosion rates and regions with very thick soils and low erosion rates, respectively. Here we attempt to move from this qualitative description to quantitative and spatially explicit predictions concerning the P status of terrestrial ecosystems.

MODEL FORMULATION

First, we consider the processes that make P available to ecosystems—the weathering of bedrock and the dissolution of mineral P within the soil column. The rate at which soil is produced from bedrock declines as soil thickness increases (Gilbert 1880; Heimsath and others 1997). Thus as erosion lowers the topographic surface, and the soil column thins, soil production rates increase, the soil/bedrock interface propagates downward, and more mineral P is incorporated into the soil column. Conversely, if erosion slows, the soil column thickens, and the soil/bedrock interface propagates downward more slowly. If erosional lowering of the surface (ϵ) is accompanied by a commensurate lowering of the bedrock/soil interface, the rate of change of the molar concentration of the reactant mineral [dq/dt ($\text{mol l}^{-3} \text{t}^{-1}$)] may be expressed as a function of:

ϵ , the erosional lowering of the surface (l t^{-1}) and assumed lowering rate of the bedrock soil interface;

kA , the product of the mineral dissolution constant k ($\text{l}^{-2} \text{t}^{-1}$) and the mineral surface area A (l^{-2});

q , the concentration of the reactant mineral in the soil column (mol l^{-3}); and

dq/dz , the vertical concentration gradient of the reactant mineral (mol l^{-4}) such that:

$$\frac{dq}{dt} = -kAq - \epsilon \frac{dq}{dz} \quad (1)$$

where z (l) is the elevation above the bottom of the weathering zone (Waldbauer and Chamberlain 2005; Chamberlain and others 2005). It should be noted that weathering zone may extend beneath the soil column, but for the purposes of this paper we use the terms “soil column” and “weathering zone” equivalently. The first term on the right-hand side of equation (1) describes the influence of the weathering reaction kinetics, and captures changes in concentration of a reactant mineral in the absence of any additional inputs from bedrock. The second term represents advection of material through the soil column via erosion and lowering of the bedrock/soil interface. The removal of material from the surface, via erosion, and the downward propagation of the weathering zone, creates advection which effectively transports material from the base of the weathering zone to the soil surface. In this formulation, the effect of erosion rates enter via ϵ , whereas soil pH, Eh, temperature, and hydrologic conditions enter via kA (Brantley and White 2003; Guidry and Mackenzie 2003). In many cases erosion rates equilibrate with tectonic

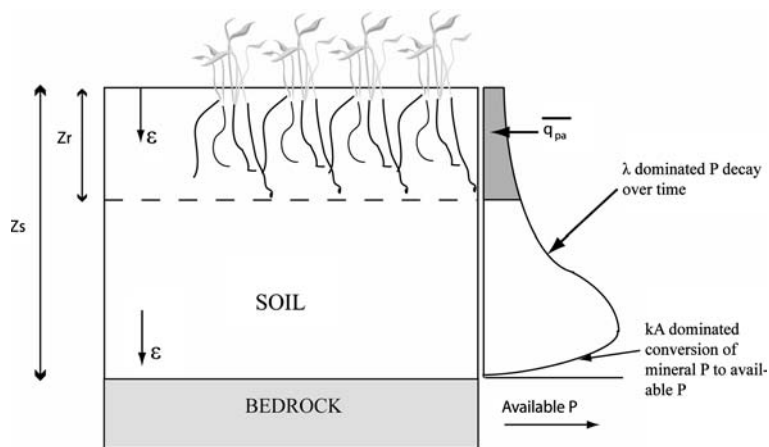


Figure 1. Schematic representation of the parameters included in the model: ϵ (the soil surface and bedrock/soil interface lowering rate), Z_s (weathering zone thickness), Z_r (rooting zone depth), kA (the dissolution rate of mineral P into available P), r (the ratio of mineral P dissolved to available P present in the soil on short timescales), λ (the decay of available P over time due to occlusion, loss, and sorption to secondary minerals), and q_0 (the concentration of mineral P in the bedrock). The model is based on the assumption that Z_s remains constant over time and that all other parameters are constant within the weathering zone. The parameters determine the average concentration of available P within the rooting zone (\bar{q}_{pa} in our model).

uplift, so in this context tectonic processes ultimately control ϵ .

In the simple case that ϵ is equal to the downward propagation of the soil/bedrock interface, the thickness of the soil (Z_s) does not change with time (Carson and Kirkby; 1972). Additionally, when $dq/dt = 0$, the concentration of P made available at the soil surface [q_p (mol l⁻³)] is:

$$q_p = r q_0 \left[1 - \exp \left(-kA \frac{Z_s}{\epsilon} \right) \right] \quad (2)$$

where r is the ratio of product to reactant, and q_0 (mol l⁻³) is the molar concentration of P in the unweathered bedrock. In our formulation, r incorporates two processes (1) the stoichiometric dissolution of reactant to product, which is three in the case of apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{F,Cl,OH})$) dissolving to form phosphate ions and (2) the immediate loss of weathered phosphate into insoluble and other largely unavailable forms. This latter process drives r to values much less than one. For example, a rock may contain 200 mol m⁻³ P, and apatite may disappear early in soil development, but soil measurements of available P never reach 200 mol m⁻³ because of rapid adsorption to secondary minerals. Thus, r is the ratio of maximum available P to the amount of P originally contained in the parent material.

Equation (2) describes the changes in concentration of available P within the soil column that result from erosion and mineral dissolution, but it does not account for the gradual loss of P or the conversion of P from available to occluded forms (Walker and

Syers 1976; Cross and Schlesinger 1995; Johnson and others 2003). To account for these well-documented transformations (Crews and others 1995; Vitousek 2004), we assume that available P decreases exponentially with time in the soil column. We represent these removal processes by introducing an empirically determined decay factor [λ (1/t)] and use it to estimate the concentration of available P at each point within the soil column:

$$q_{pa} = r q_0 \exp(-\lambda t) \left[1 - \exp(-kA Z_s / \epsilon) \right] \quad (3)$$

where q_{pa} (mol l⁻³) is the molar concentration of biologically available P at point z , and t is the time since the parcel of mineral P at depth z entered the weathering zone. The decay term (λ) describes the processes that affect the concentration of available P as it remains in the soil: the occlusion, adsorption, and loss of available P over time and the changes in concentration of available P associated with soil collapse or expansion during formation. As the time since mineral P entered the soil column is the effective soil age ($\tau = z/\epsilon$), equation (3) may be written as

$$q_{pa} = r q_0 \exp(-\lambda z / \epsilon) - ((-kA - \lambda) z / \epsilon) \quad (4)$$

Equation (4) represents the concentration of available P at each point in the soil column given an erosion rate ϵ . Plants gather nutrients within the upper portion of the soil, and thus we introduce a term that represents the thickness of the rooting zone [Z_r (m)]. We integrate equation (4) between the elevation of the surface (Z_s) and the bottom of

the rooting zone ($Z_s - Z_r$) and divide by Z_r to arrive at an average concentration of available P ($\overline{q_{pa}}$ mol l⁻³) within the rooting zone for a given values of r , q_0 , λ , kA , and τ (Z_s/ϵ):

$$\overline{q_{pa}} = \frac{\int_{(Z_s - Z_r)}^{Z_s} q_{pa} (dz)}{Z_r} \quad (5)$$

The solution of equation (5) is included in Appendix 1 (see <http://www.springerlink.com>).

The six parameters in our model represent the length (Z_s , Z_r) and timescales (kA , λ , ϵ) and ratios (r) that determine P availability in ecosystems. To explore the importance of relative length and timescales, we recast the integration of equation (5) in nondimensional form (Appendix 1 at <http://www.springerlink.com>). Phosphorus availability to ecosystems depends on the proportion of the soil that is exploited by plants for nutrient uptake, especially where deep rooting or extensive mycorrhizal symbioses are common plant strategies (Nepstad and others 1994; Jackson and others 1999). In our nondimensional formulation, we express the rooting zone depth as a fraction of the total soil depth ($Z^* = Z_r/Z_s$), and allow this to vary between 1 and 99%. Phosphorus availability also depends on the relative rates of apatite dissolution and loss of available P; thus we define λ^* as the ratio of these rates (λ/kA). We obtained realistic ranges for λ^* from the model calibration discussed below. The relative rate of apatite dissolution and soil residence times also determines P availability, so we recast τ in the nondimensional form $\tau^* = kAZ_s/\epsilon$. In the nondimensional model, we set $r = 1$, since r is a linear scaling factor that does not affect the relative P availability between soils of different residence times.

MODEL CALIBRATION

Although nondimensional equations allow us to explore the behavior of the model across a range of parameters, we were interested in understanding how the parameters, and thus predictions of P availability, varied among real ecosystems. To address this issue, we made the assumption that the age of chronosequence surfaces could be substituted for the residence time of the soil (τ), and further assumed that soil measurements of available P could be used as a proxy for our modeled available P ($\overline{q_{pa}}$). This allowed us to use available phosphorus data from three chronosequences for which soil ages are reasonably well known to derive plausible estimates of r , kA , and λ (for clarity, we will use $\overline{q_{pa}}$ when

discussing model results and “available P” with regards to field-based measurements). This approach was necessary because λ has not been directly measured in the field, and although apatite dissolution has been measured in reactor experiments, the results are sensitive to changes in pH (Guidry and Mackenzie 2003) and often conflict with field estimates (Brantley and White 2003). Moreover, to our knowledge there have been no explicit estimates of r , the fraction of apatite dissolution that becomes available over short timescales.

The three chronosequences we chose are the Hawaiian long substrate age gradient (hereafter LSAG; Crews and others 1995), a wetter Hawaiian chronosequence (hereafter Wet LSAG), and the Franz Joseph Chronosequence in New Zealand (hereafter Franz Joseph; Stevens 1968). The LSAG sites are located on basaltic lavas and tephros that range in age from 300 to 4.1×10^6 year and contain approximately 200 mol P m⁻³. They sit atop minimally eroded surfaces, have a mean annual temperature (MAT) of approximately 16°C, a mean annual precipitation (MAP) of approximately 2.5 m y⁻¹, and are dominated (>75% of stems) by the same species of tree (Vitousek 2004). Across the LSAG, the soils progress from Andisols at the young and intermediate-aged sites to Oxisols at the oldest, pH in the A horizon drops from approximately five to four across the sequence, and organic carbon increases with age (for example, from ~10 to ~25% in the upper A horizon—O. A. Chadwick, unpublished data). The Wet LSAG sites are situated on similar substrate that ranges from 200 to 4.1×10^6 year, and the sites have similar state factors (*sensu* Jenny 1941) to the LSAG, but receive approximately 4 m y⁻¹ rainfall. The young soils along this chronosequence are similar to the LSAG, but after 1.5×10^5 year the sites are dominated by boggy Histosols. Soil pH ranges from approximately six at the young site to approximately four at the oldest, and soil organic matter accumulates to over 50% of the upper 40 cm at the oldest site (O.A. Chadwick, unpublished data).

The Franz Joseph chronosequence, on the west side of the South Island of New Zealand, is situated on a series of river and kame terraces composed primarily of greywacke detritus (Stevens 1968). The ages of the surfaces we included in this study range from 100 to 1.2×10^5 year, with dating of the oldest sites based on correlation with known glaciations in the New Zealand Alps (Stevens 1968; Almond and others 2001). MAT is 11°C and MAP ranges from approximately 6 m y⁻¹ at the younger sites to approximately 3 m y⁻¹ at the oldest. Although the sites we selected are dominated by

Table 1. Descriptions of the Three Chronosequences used to Empirically Determine kA (Mineral P Dissolution Rate), r (Ratio of Mineral P to Dissolved Available P), and λ (Rate of Decay of Available P within the Soil Column Over Time)

	LSAG	Wet LSAG	Franz Joseph
Location	Hawai'i, USA	Hawai'i, USA	South Westland, New Zealand
Parent material	Basalt	Basalt	Greywacke outwash
Topography	Flat volcanic shield surface	Flat volcanic shield surface	Flat glacial terraces
Age range (years)	300–4.1 × 10 ⁶	200–4.1 × 10 ⁶	100–1.2 × 10 ⁵ ¹
Dominant species	<i>Metrosideros polymorpha</i>	<i>M. polymorpha</i>	Mixed angiosperm/ conifer forest
Rainfall (m y ⁻¹)	2.5	4	3–6 ²
Youngest soil	Hapludand (Andisol)	Andic dystropepts (Inceptisol)	Sandy loam ³
Intermediate soils	Hydrudand (Andisol)	Epiaquands (Andisol)	Peaty loam ³
Oldest soil	Kandiudox (Oxisol)	Haplosaprists (Histosol)	Clay rich loam ³
Available P	Resin + bicarbonate P, NaOH Po	Resin + bicarbonate P, NaOH Po	NH ₄ Cl, NH ₄ F Pi, 50% Po
Substrate (P)	200 mol m ⁻³	200 mol m ⁻³	38 mol m ⁻³
P limitation threshold	5.2 mol m ⁻³	5.2 mol m ⁻³	0.86 mol m ⁻³

¹ Only data from stages VII and older (after Stevens 1968) were used for this analysis.

² The youngest three sites receive 6 m y⁻¹, the oldest three sites receive 3 m y⁻¹ (Richardson and others 2004).

³ Soil descriptions from Stevens (1968). Modern soil classifications are unavailable.

mature forest, there is more variation in species composition than across either of the Hawaiian chronosequences (Stevens 1968; Richardson and others 2004). The soils are sandy loams with a large fraction of rock fragments at the youngest sites, humic rich “peaty loams” at the 1.2 × 10⁴ year site, and low porosity silt and clay rich soils at the oldest (1.2 × 10⁵ year; Stevens 1968; Almond 2001). The oldest two sites exhibit pronounced gleying and podsolization (Stevens 1968). Soil pH drops from approximately five to approximately four and soil organic carbon accumulates from 2 to 5% in the upper soil from the youngest to oldest sites (Stevens 1968). Because parent material P concentrations have not been reported, we use the global average composition of greywackes (700 ppm P—Taylor and McClennan 1985) and bulk density of till of 1.7 g cm⁻³ (Calhoun and others 2001) to estimate the initial concentration of P in the parent material ($q_0 = 38 \text{ mol P m}^{-3}$). The three chronosequences are compared in Table 1.

Sites along these chronosequences were deliberately placed on flat, minimally eroded surfaces, and so we approximate $\epsilon = 0$. Thus, we can simplify equation (1) by eliminating the advection term such that:

$$\frac{dq}{dt} = -kAq \quad (6)$$

Substituting site age (t) for the effective surface age (Z_s/ϵ), and following the same steps that produced equations (2)–(4) yields

$$\overline{q_{pa}} = rq_0 [\exp(-\lambda t) - \exp((-kA - \lambda)t)] \quad (7)$$

We used equation 7, the relationship between measured available P and time across each chronosequence, q_0 measured from bedrock values, and r from the ratio of q_0 to the maximum available P along each chronosequence to estimate r , kA , and λ under the different lithologic and climatologic conditions represented by the chronosequences. We assumed that these parameters did not vary across a given chronosequence, and compared observed and predicted values of available P for specific choices of kA and λ . We then varied kA and λ to achieve the best-fit model curve using a non-linear optimization algorithm (Dennis 1977). This technique was repeated for each chronosequence to understand how kA and λ varied with differences in lithology and climate.

We recognize that other chronosequences have been studied; we selected these three for a number of reasons. The LSAG was chosen because it is an intensively studied chronosequence for which the appropriate soil P data were available, as were fertilization data that demonstrate P limitation at the oldest site. Both LSAG sequences span the longest timescale of any well-studied chronosequence. The Franz Joseph chronosequence was chosen because it was the only series of sites on aluminosilicate rich rocks that spanned a timescale of over 10⁵ year and was wet enough that soil development might proceed as a result of soil weathering, rather than wind ablation and dust

deposition as in drier environments (for example, Lajtha and Schlesinger 1988). Nevertheless, dust deposition is likely greater along the New Zealand chronosequence than in Hawai'i, a problem shared by any well-studied chronosequence on continental material (see below).

MODEL LIMITATIONS

Our model is a first step toward quantifying the major processes involved in determining P availability to ecosystems. Nevertheless, there are several assumptions that need to be considered, both in the conceptualization of the model and in the use of chronosequences to estimate model parameters.

We assume that kA and λ are constant across a given chronosequence, and from the bottom to the top of the soil column. Although this is a reasonable place to start, in reality variation in pH, soil mineralogy, and biological activity causes both properties to change with age across chronosequences and with depth in soil columns. For example, as pH drops, mineral weathering rates will increase (Guidry and Mackenzie 2003). Soil minerals differ in their P binding capacities, which means that λ may vary as well. Understanding how these parameters vary throughout the soil column will help to refine our model in the future.

Atmospheric deposition of P occurs to some extent in all ecosystems. Even in Hawai'i, which is one of the least dusty places in the northern hemisphere, dust is a significant input of P at the older sites (Kurtz and others 2001). In New Zealand, loess deposition during glaciations can be substantial (Stevens 1968), although the P input via loess to the Franz Joseph has not been quantified. The input of dust means that available P data from any chronosequence reflect not only just rock weathering and P decay, but also exogenous inputs of P over time. Cumulative atmospheric deposition may be especially important for sites old enough to have experienced full glacial conditions (Kurtz and others 2001).

We assume that P availability to ecosystems can be measured by soil extractions. There is an extensive literature on the various chemical extraction techniques that best capture the P available to biota, but all extraction techniques are at best a proxy (Cross and Schlesinger 1995; Johnson and others 2003). For the LSAG and wet LSAG data, we followed the classification by Johnson and others (2003) of P "available to plants over the growing season", and included resin P, bicarbonate extractable P, and NaOH extractable organic P. We have confidence that this extraction

captures the trends in P availability across the Hawaiian chronosequences because similar trends are seen in leaf nutrient concentrations and productivity (Vitousek 2004).

Unfortunately, the most detailed study of the Franz Joseph used a different set of chemical extractions, and organic P was not separated into different pools (Stevens 1968). Hence, we use the two mildest inorganic extractions (NH_4Cl and NH_4F), and assume that 50% of the total organic P is in the NaOH extractable pool. This is a conservative estimate for both inorganic and organic P availability. Bray's extractable P, which is commonly thought to be available to plants, includes a similar NH_4F component (Bray and Kurtz 1945; Stevens 1968). Approximately 75% of organically bound P across the LSAG is in the NaOH extractable pool. Compared with the mafic parent material in Hawai'i, the glacial till parent material of the Franz Joseph sites has fewer P sorbing iron and aluminum oxides (Efimov and others 1996; Pant and Reddy 2001), and thus a greater fraction of organic P is likely in a relatively available pool, making our 50% estimate conservative as well. Leaf measurements across the Franz Joseph show a decline in P over time (similar to the soil data; Richardson and others 2005). As the above discussion indicates, our understanding of which soil pools are available to ecosystems, and over what timescales, is in need of substantial refinement. Nevertheless, our available P data capture the predicted rise and fall of available P over time (see Results). Finally, the absolute value of measured available P is less important for our model, as it is incorporated into the scaling factor r .

We assume that the timescale of apatite dissolution (kA) and available-P loss (λ) are large relative to any lags between surface formation and mineral weathering. Because we have data for the top 50, 75, and 100 cm for the LSAG, Franz Joseph, and Wet LSAG, respectively, we believe that this assumption is reasonable at the oldest sites, although it is not likely to be true at the youngest. Because we are primarily concerned with long-term P depletion this assumption is unlikely to unduly influence our results, but a transient rather than steady-state model will be an important next step.

We assume that plants along these chronosequences gather nutrients from the depths for which we have soil P data. In part this is an assumption based on necessity, but most roots across the LSAG are in the upper 50 cm of soil (Ostertag 2001). Studies of rooting depth are not available for the Wet LSAG (although the rooting zone appears shallower than the more mesic sequence) or Franz Joseph.

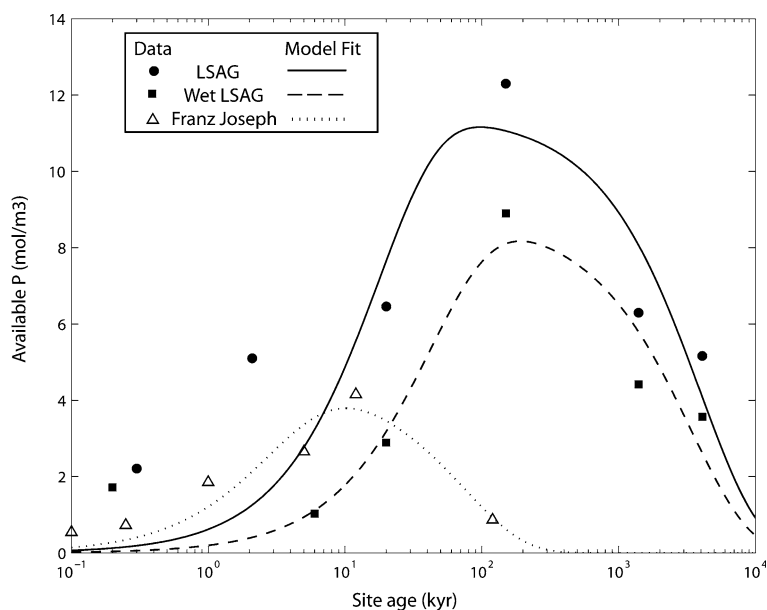


Figure 2. The variation in available P with site age (in thousands of years, kyr) for the LSAG, Wet LSAG, and Franz Joseph chronosequences. For the two Hawaiian chronosequences, available P is equivalent to the pool available over the growing season, as defined in Johnson and others (2003) (labile P, bicarbonate extractable P, and NaOH extractable organic P) and is from analysis of the upper 50 and 100 cm for the LSAG and Wet LSAG respectively (P data from Crews and others 1995; T. Crews unpublished data; Oliver Chadwick, unpublished data). For the Franz Joseph, available P includes NH_4Cl , NH_4F and 50% of the organic P fraction to a depth of 75 cm as reported by Stevens (1968). Site ages for the Franz Joseph are from Stevens (1968) and Almond (2001).

RESULTS

Model Calibration

All three chronosequences have approximately $8\times$ variation in measured available P, which increases and then decreases with time (Figure 2). LSAG and Wet LSAG P availability peaks at 1.5×10^5 year (12.3 and 8.9 mol m^{-3} , respectively), whereas Franz Joseph P availability is highest at 1.2×10^4 year (4.2 mol m^{-3}). As a result, our best-fit estimation of kA is an order of magnitude faster for the Franz Joseph than the Hawaiian chronosequences, and λ is two orders of magnitude faster (Table 2). The Hawaiian sequences are not substantially different from each other, and thus we combined them for the remainder of the analyses. r from all three sequences is similar, and indicates that the majority of available P produced by mineral dissolution is rapidly immobilized into relatively unavailable forms.

Nondimensional Model

In areas with high uplift rates and thin soils (small τ^*), the movement of particles through the soil column is too rapid for mineral P dissolution (kA) to produce high \bar{q}_{pa} independent of variation in λ or Z_r (Figure 3). In slowly uplifting regions with deep soils (large τ^*), apatite dissolution occurs deep in the soil column, and \bar{q}_{pa} is reduced by the decay of P availability with time (λ). Thus, the nondimensional model generates a prediction of low P availability in soils with both very small and very large τ^* , which is in concordance with measurements of low available P both on very young and

on old uneroded soils (Chapin and others 1994; Vitousek and Farrington 1997). P limitation to primary production can be observed in both of these situations—in young sites where biological N fixation supplies enough N to offset the N limitation that would otherwise be anticipated (Chapin and others 1994) and in old systems with deep soils and negligible advection (Vitousek and Farrington 1997).

Using the range of λ^* observed between the chronosequences (Table 2), we calculate that an order of magnitude difference in λ^* produces almost two orders of magnitude of variation in the τ^* at which \bar{q}_{pa} decreases to near zero (Figure 3a). Thus, the ratio of the apatite dissolution rate to the decay rate of available P is likely to play a large role in determining whether a region is P depleted. The relative timescales of λ and kA (λ^*) also affect the maximum \bar{q}_{pa} . As the two timescales approach each other, the maximum \bar{q}_{pa} is diminished as decay occurs contemporaneously with apatite dissolution (see the curve for $\lambda^* = 0.05$; Figure 3a). Our best fit data from the chronosequences indicates that the decay of available P is at least an order of magnitude slower than the dissolution of mineral P, but given the large effect variation in λ^* has on P availability; these parameters should be investigated in other ecosystems, particularly on different parent materials that will produce soils with different P binding capacities.

In contrast to λ^* , variation in the ratio of rooting depth to soil depth (Z^*) has a much smaller effect on \bar{q}_{pa} unless Z^* approaches 1, an unlikely scenario in regions with deep soils (Figure 3b). Thus, the difference between plants gathering P from 1%

Table 2. kA , r , and λ Derived from Available P Versus Time Data Across the Three Chronosequences

	kA (ky^{-1})	r	λ (ky^{-1})	R^2
LSAG	5.53×10^{-2}	0.058	2.53×10^{-4}	0.74
Wet LSAG	2.27×10^{-2}	0.044	2.95×10^{-4}	0.87
Franz Joseph	3.16×10^{-1}	0.121	1.32×10^{-2}	0.89

For the Hawaiian chronosequences, the concentration of P in rock ($q_0 = 200 \text{ mol m}^{-3}$) is the average of several Hawaiian basalts. For the Franz Joseph we assume $q_0 = 38 \text{ mol m}^{-3}$ based on average concentrations for greywacke and bulk densities for glacial till (see References in text). The R^2 statistic shows the variation in available P.

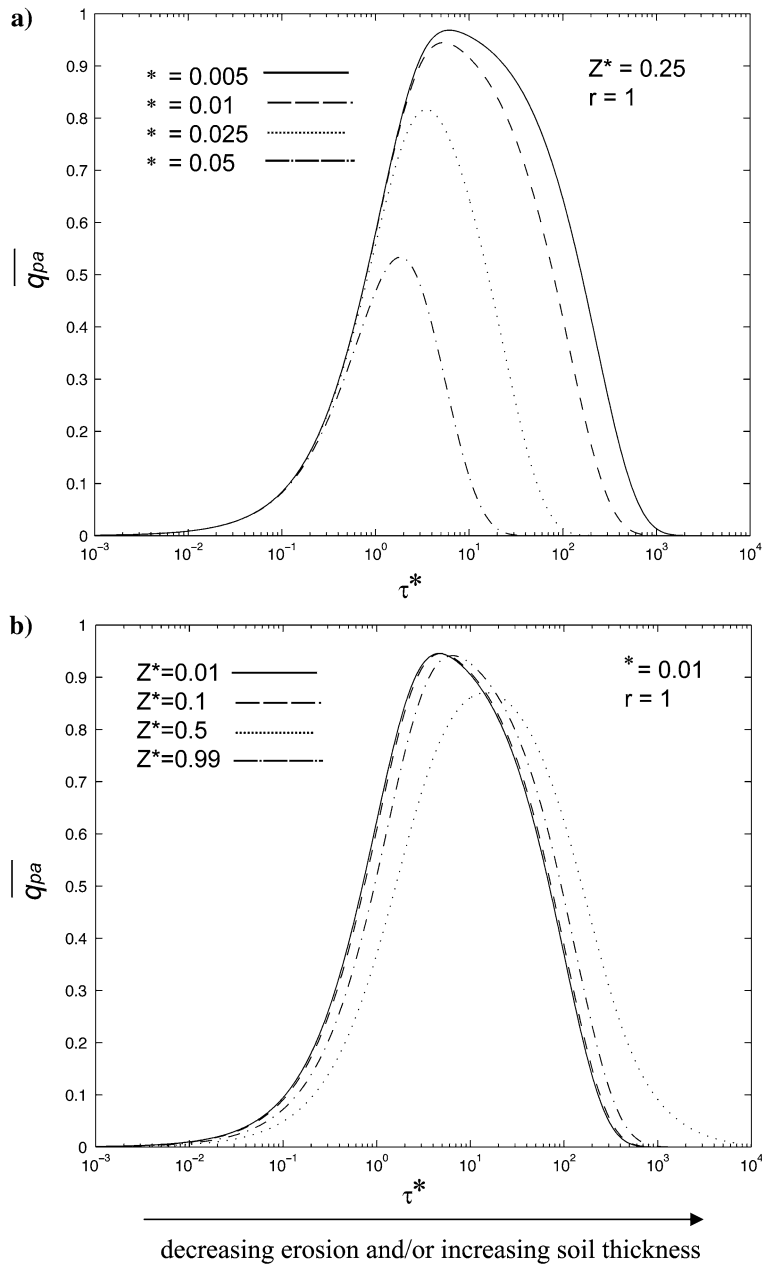


Figure 3. The effects of the rate of P loss and rooting zone thickness on predictions of P availability. **a** τ^* vs. modeled available P for different values of λ^* . τ^* is the product of soil residence time (τ) and the mineral dissolution rate (kA). λ^* is the ratio of P decay (λ) to kA . **b** τ^* vs. $\overline{q_{pa}}$ for different values of Z^* (the ratio of rooting depth to soil depth). r , the stoichiometric ratio of mineral P to dissolution product (available P), is set to one.

versus 50% of the soil shifts the τ^* at which $\overline{q_{pa}}$ approaches zero by a factor of less than 2. This is not to suggest that rooting depth is an unimportant

variable, but rather that kA and λ are likely the more important determinants of ecosystem P status in regions with deep soils.

Spatial Variation in P Availability

We were particularly interested in understanding how P availability varied spatially across the terrestrial biosphere, and used available data to predict soil residence times in different tectonic settings. Having arrived at empirical determinations of r , kA , and λ , we assumed that erosion rates are balanced by tectonic uplift in many landscapes (for example, Whipple and others 1999). Thus, we set uplift [U ($l\ t^{-1}$)] equal to ϵ , and gathered data from the literature on U and soil depth to bedrock (assumed to be equal to Z_s) in different locations. Reported uplift rates ranged from 10^{-3} to $10\ m\ ky^{-1}$, although zero uplift and subsidence exist in natural systems. Soil depths were reported more haphazardly, but ranged from 0 to 100 m (Appendix 2, see <http://www.springerlink.com>). We grouped these data into five tectonic settings: collisional mountain belts (for example, the Himalaya), subduction zone uplift regions (for example, Western South America), inactive mountain belts (for example, the Appalachians), glaciated cratons (for example, the Central Canada), and unglaciated cratons (for example, the Amazon Basin). Using the reported range in soil depths and uplift rates, and substituting tectonic uplift rates (U) for erosion rates (ϵ) in our model, we calculated the expected \bar{q}_{pa} in these tectonic settings.

The large difference between the Hawaiian and Franz Joseph chronosequences translate into very different predictions about the extent of P depletion in lowland tropical forests (Figure 4). This extent is lowest if the parameters derived from Hawai'i are indicative of much of the continental tropics. The decline of available P in Hawai'i takes millions of years, and there are few regions with residence times long enough to experience the terminal P depletion seen at the oldest LSAG sites. In contrast, if the Franz Joseph parameters are more representative, P depletion occurs more quickly and therefore is likely to be more widespread. However, using parameters from either chronosequence, we see that long-term P depletion is restricted to stable tectonic settings where advection is slow, and is unlikely to occur where tectonic activity results in even moderate uplift and erosion (Figure 4).

To explore where P depletion might be expected to result in limitation to plant productivity by P, we used the results of a fertilization experiment along the LSAG that demonstrated P limitation to primary productivity at the 4.1×10^6 year LSAG site, where available $P = 5.2\ mol\ m^{-3}$ (Crews and others 1995; Herbert and Fownes 1995; T. Crews, unpublished data). We use this value as a conser-

vative threshold below which we expect P limitation to occur on iron rich volcanic soils. Although no fertilization experiment has been carried out on the Franz Joseph, leaf nutrient ratios have been used to argue that P limitation occurs at the oldest site (1.2×10^5 year) as well (Richardson and others 2004). Although we do not accept that leaf nutrient ratios are proof of nutrient limitation, we use the reported value of available P from this site (available $P = 0.9\ mol\ m^{-3}$; Stevens 1968) as a first cut for the threshold for P limitation on aluminosilicate-rich parent material under similar climatic conditions. As mentioned earlier, although the difference in available P values may reflect the lithologic differences between the LSAG and Franz Joseph, it is more likely a result of the difference in extraction procedure used to determine available P concentrations. Nevertheless, the use of these values allows us to explore where P limitation may occur in a Hawai'i-like or Franz Joseph-like world.

The Hawai'i-derived parameters generate a prediction that among older sites, *only* stable cratons with low uplift/erosion rates are likely to experience long-term P limitation. In much of the rest of the tropics, uplift rates are too high to produce P depletion except in the case of extraordinarily deep soils (Figure 5a). For example, an unrealistic soil depth of almost 10^3 m is needed to produce P limitation even at the relatively slow uplift rate of $0.01\ m\ ky^{-1}$. In contrast, the Franz Joseph-derived parameters, which are indicative of faster P loss, lead to the prediction that P limitation may occur for soils over approximately 10 m deep at this same uplift rate (Figure 5b). Even using these parameters, which are indicative of faster P decay, we predict that in many tropical settings (for example, Central American or Southeast Asia), uplift rates are fast enough ($>0.1\ m\ ky^{-1}$) to make P limitation unlikely.

DISCUSSION

Our model captures the expected rise and fall of P availability over time, and indicates that variation in soil residence times may be a key determinant of P availability to ecosystems. Our incorporation of a soil advection term indicates that only tectonically stable regions, with low uplift and erosion rates, are likely to experience long-term P depletion. Mineral dissolution rates, as well as the time it takes for available P to be lost from the biologically available pool, also represent an important control. In contrast, although plants may employ deep roots for water and nutrient uptake in a variety of ecosystems (Nepstad and others 1994; Jackson and others

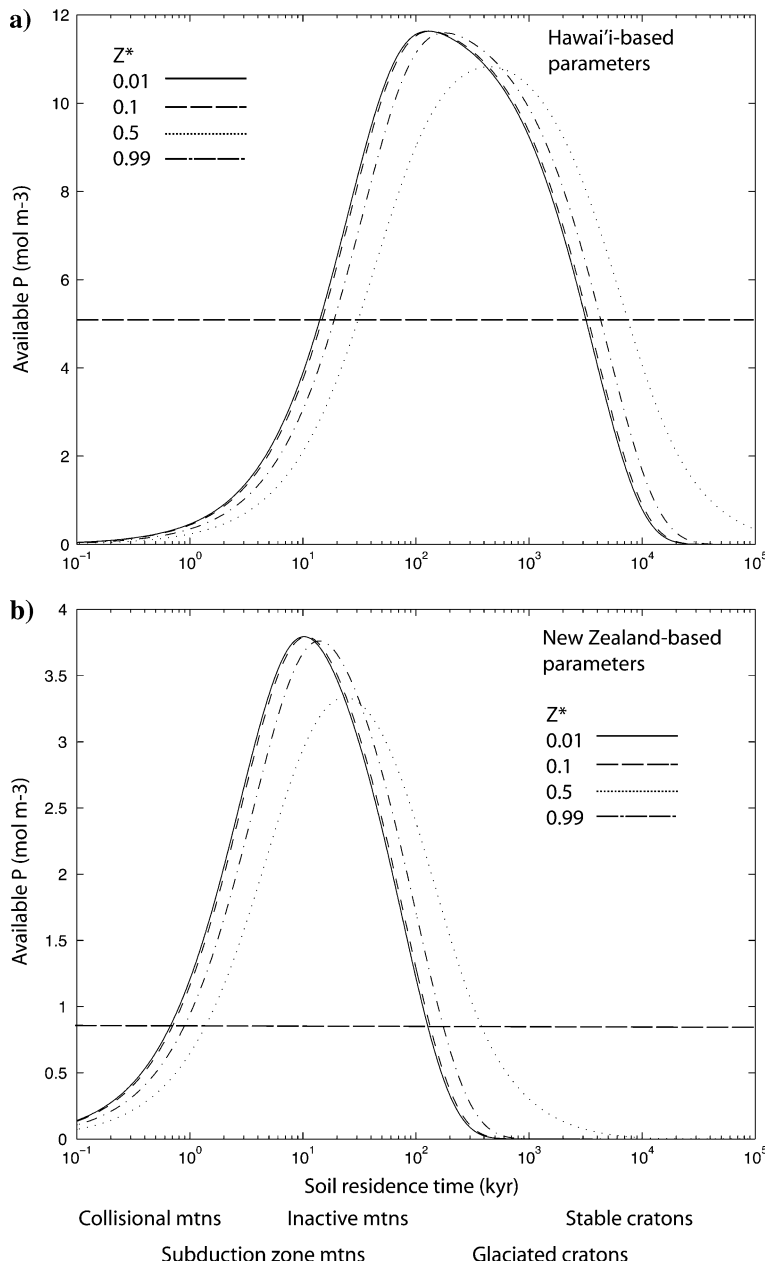


Figure 4. Predicted variation in available P in regions with different soil residence times $\tau = Z_s/U$ (kyr). **a** The variation predicted for a world where kA , r and λ are the average of those derived from Hawaiian chronosequences. The *horizontal dashed line* shows the concentration of available P on the top 50 cm of soil at the oldest, experimentally determined P limited site. **b** The variation predicted using parameters derived from the Franz Joseph chronosequence. The *horizontal dashed line* shows the concentration of available P in the upper 75 cm at the oldest, putatively P limited site. The range in τ for different tectonic settings is shown at the *bottom*, and is drawn from sources listed in Appendix 2 (see <http://www.springer-link.com>).

1999), the model indicates that rooting depth is not as important a control of ecosystem P status in regions with deep soils. Although we do not examine the short timescale processes that determine P availability, root distribution, decomposition, nutrient use efficiency, and so forth, our model does capture some of the long-term dynamics that control the ultimate amount of P that is accessible to organisms in different tectonic settings.

These results are predicated on the assumption that soil thickness does not vary with time—and our predictions for the P status of different tectonic regions also assume that erosion is balanced by tectonic uplift. These assumptions may be valid for

many landscapes over geologic timescales (Whipple and others 1999; Willett and others 2001), but it is not clear that the same is always true over shorter, ecologically important timescales (tens to hundreds of thousands of years). For example, landslides occurring every few thousand years can occur in a “steady state” geologic landscape, but the system may never reach steady state in terms of soil nutrient availability. However, such events may further decrease the extent of P depletion in the tropics, because erosion can increase the supply of rock-derived P (Vitousek and others 2003; Porder and others 2005a; Porder and others 2005b). The development of a model that does not rely on a

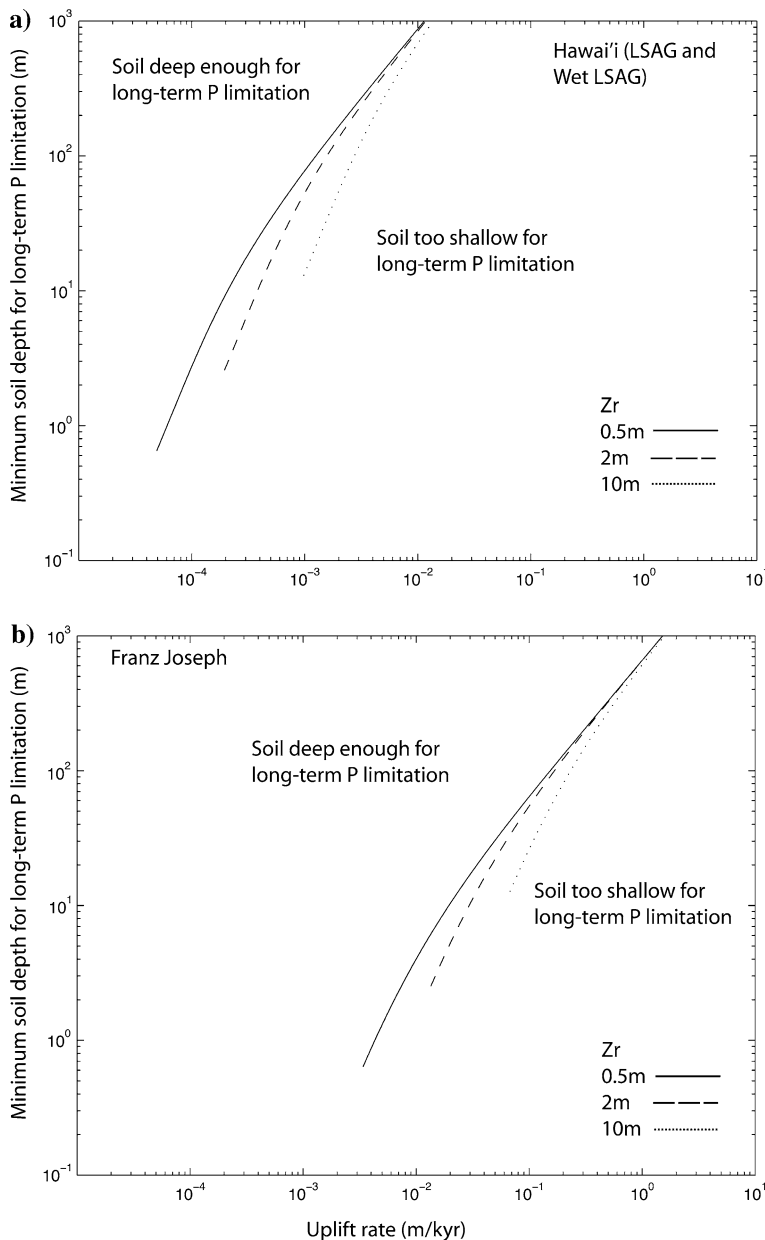


Figure 5. The minimum soil depth required to achieve P limitation for different τ and rooting depths (Z_r). P limitation is assumed to exist where concentrations of available P are below those found at the oldest, P-limited chronosequence sites. **a** Minimum depth of soil required to generate P limitation using parameters (kA, r, λ) from the average of those derived from the Hawaiian chronosequences. **b** Minimum depth of soil required to generate P limitation using parameters (kA, r, λ) derived from the Franz Joseph chronosequence.

constant thickness weathering zone, and thus can be adapted to consider pulsed erosion events, variations in climate, and other transient phenomena is an important next step.

Furthermore, P limitation does not exist in a vacuum—it is the result of a stoichiometric deficiency of P relative to other nutrients. For example, a more rapid build up of N might induce the onset of P limitation earlier in ecosystem development, and more rapid losses of Ca and other cations could ensure that they, rather than P, limit productivity in the oldest soils. We defined P limitation on the LSAG to occur only at the oldest, P poor site but the most fertile site (2×10^4 year) is limited by P and N

when they are supplied in combination. If we were to use this age as the onset of P limitation, it would make the predicted uplift rate necessary for P limitation similar to that derived from the Franz Joseph parameters. If we take this broader definition of P limitation, however, it seems unlikely that the long-term decay of P availability is a common cause of P limitation. For example, the intermediate-aged, N and P colimited Hawai'i site has the second highest available P along the chronosequence. It is certainly not at the terminal steady state of minimal available P that Walker and Syers (1976) described, and which has been widely interpreted as the ultimate cause of P limitation in the tropics.

Although rock is the ultimate source of P to ecosystems, proximate sources include colluvial material and atmospheric deposition (dust, rain, fog, and so forth). It can be shown that slope processes do not affect the mean residence time of soils under the model conditions described above (Hilley and others 2006), but atmospheric inputs can be important in particular cases (Stoorvogel and others 1997; Okin and others 2004)—especially in old soils on uneroded surfaces where bedrock sources of nutrients are depleted and productivity is sustained by exogenous inputs of nutrients (Chadwick and others 1999; Kurtz and others 2001). Our model is only designed to assess the influence of bedrock P inputs (although the calibration with chronosequence data unavoidably includes dust inputs) and thus predictions generated by the model should be considered baseline predictions of P-depletion in the absence of exogenous inputs of P. In this light, the prediction that long-term P depletion is largely confined to stable cratonic settings, even in the *absence* of exogenous inputs, is a conservative one.

The chronosequences on which we base our analysis are similar to many of the tropical ecosystems assumed to be limited by P; they receive 2.5–6 m y⁻¹ rainfall, and are situated on either mafic volcanics or parent material similar in chemical composition to average continental crust. Approximately 40% of the earth's terrestrial surface is underlain by rocks similar in chemical composition (Dürr and others 2005). Although variation in our model parameters needs to be quantified in multiple ecosystems, the fact that our model fails to predict P depletion for regions with moderate to high uplift rates argues for a re-evaluation of the global extent of terrestrial P limitation.

ACKNOWLEDGEMENTS

The authors would like to thank Tim Crews for his generous provision of detailed P fractions from the LSAG, and Sarah Richardson and Troy Baisden for assistance with obtaining data from the Franz Joseph. Dr. Donald DeAngelis and two anonymous reviewers provided useful comments on an earlier version of the manuscript. Funding was provided by a grant from the Stanford Institute for the Environment, Environmental Interdisciplinary Initiatives Program “Carbon Dioxide Sequestration by Forests: The Importance of Cation and Phosphorous Limitation and Its Relationship to Landscape Evolution.” This document is STGL contribution number 06–04.

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