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The effect of plants on mineral weathering

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Abstract. This paper is centered on the specific effects of plants on the soil weathering environment; we attempt to address how to quantify this component of the ecosystem and assess feedbacks between plants and weathering processes that influence the degree and rates of mineral weathering. The basic processes whereby plants directly influence the soil chemical environment is through the generation of weathering agents, biocycling of cations, and the production of biogenic minerals. Plants may indirectly influence soil processes through the alteration of regional hydrology and local soil hydrologic regime which determines the residence time of water available for weathering. We provide a brief review of the current state of knowledge regarding the effects of plants on mineral weathering and critical knowledge gaps are highlighted. We summarize approaches that may be used to help quantify the effects of plants on soil weathering such as state factor analyses, mass balance approaches, laboratory batch experiments and isotopic techniques. We assess the changes in the soil chemical environment along a tropical bioclimatic gradient and identify the possible effects of plant production on the soil mineralogical composition. We demonstrate that plants are important in the transfer of atmospheric carbon dioxide into the mineral weathering cycle and speculate how this may be related to ecosystem properties such as NPP. In the soils of Hawaiian rainforests subjected to deforestation, pasture grasses appear to change the proportion of non crystalline to crystalline minerals by altering the soil hydrologic regime or partitioning silica into more stable biogenic forms. A better understanding of the relationship between soil weathering processes and ecosystem productivity will assist in the construction predictive models capable of evaluating the sensitivity of biogeochemical cycles to perturbations.

Introduction

Soils have drawn intense interest worldwide because they are recognized as a critical component in the biogeochemistry of terrestrial ecosystems. Scientists from many disciplines are now seeking quantitative information about key soil processes that augment regional and global biogeochemical cycles. Geological, ecological and pedological investigations, utilizing different approaches and methods, have all demonstrated that the relative importance of plants in regulating weathering processes is dependent on the temporal scale of observation (Jackson & Keller 1970a,b; Berner 1992; Cochran & Berner 1992; Warfvinge & Sverdrup 1992; Drever 1994). In soils that are primarily

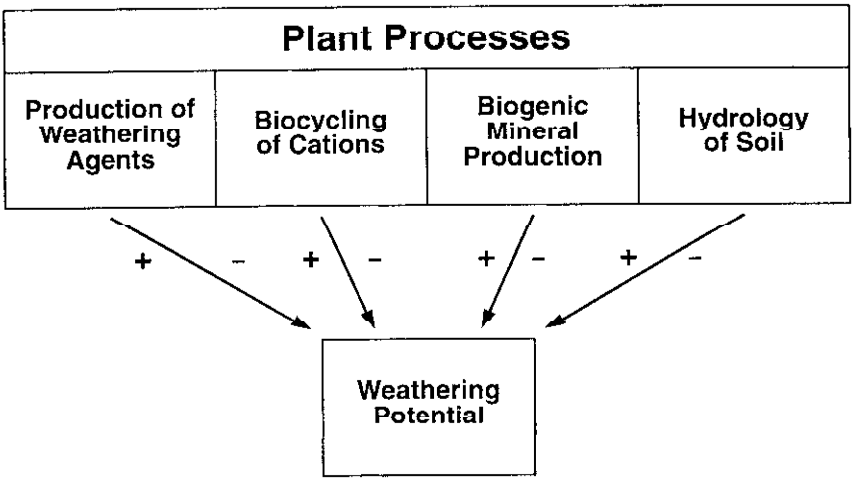

Figure 1. Overview of plant processes that influence weathering potential of soils; + = positive feedback; – = negative feedback.

composed of mineral material, chemical and physical weathering processes regulate nutrient levels (Vitousek 1995), consumption of atmospheric carbon dioxide (Berner 1992; Chadwick et al. 1994a), the chemical composition of surface and ground waters (Benedetti et al. 1992) and the physical and chemical behavior of soil (Jackson 1958; Jenny 1980; Birkeland 1984).

The key questions regarding the effects of plants on mineral weathering include: (1) How can the influence of plants on mineral weathering be quantified?, (2) How do plants affect mineral weathering processes?, and (3) Can weathering processes be linked to key biological properties of the ecosystems? We focus our review on four critical groups of plant related processes, namely, the production of weathering agents, biocycling of cations, production of biogenic minerals, and the hydrology of soils (Figure 1). These processes and feedbacks can be evaluated in terms of their weathering potential. Feedbacks exist between sets of processes which can increase (+) or decrease (–) the weathering potential of the process. If a specific process or set of processes are considered to provide a positive (+) feedback they will increase weathering, whereas negative (–) feedbacks are likely to decrease weathering. Some sets of plant processes may provide both positive and negative feedbacks depending on external factors which are conditioned by bioclimatic, geologic and pedologic conditions. These factors strongly influence the relative importance of each set of plant processes and type of feedback.

The most recent and significant attempts to link plants to weathering processes has been made by scientists modeling the global C cycle on geologic time scales (Berner 1992; Cochran & Berner 1992; Drever 1994). At this temporal scale (up to hundreds of millions of years) the chemical weathering of Ca- and Mg-rich silicate rocks is considered to be the principal process whereby atmospheric CO_2 is transferred through the terrestrial system back to the oceans and generally follows the stoichiometric relationships of silicate dissolution and oceanic carbonate precipitation (Berner 1992). These estimates of long-term weathering have relied mostly on experimental data and modeling with the assumption that soil pH is controlled by equilibration of atmospheric CO_2. In most of these assessments the landscape is treated as a single homogenous unit, as is the soil or bulk solution. Rhizosphere effects on pH, which may be significantly different from the bulk solution are generally ignored. Much of the information regarding these calculations is based on an incomplete knowledge of weathering processes in modern plant and soil systems. For example, the debate continues on the relative importance of primitive plants (lichens and or algae) versus vascular plants and their influence on soil weathering (Jackson 1958; Jackson & Keller 1970a,b; Cochran & Berner 1992; Jackson 1996). Deeply rooted expansive forest ecosystems are believed to have spread across the continental areas during the late Silurian and early Devonian (Alego et al. 1995) the consequences of which may have been quite significant for carbonic acid weathering and the coevolution of soil and terrestrial ecosystems (Richter & Markewitz 1995).

At shorter time scales that cover plant succession, investigations of soil weathering generally focuses on how weathering processes influence the storage of nutrients available to plants because nutrient availability is an important constraint upon ecosystem productivity (Vitousek et al. 1995). In general, the major inputs of nutrients into the soil are from mineral weathering and atmospheric deposition (precipitation and dry fallout). Quantifying the degree to which weathering supports nutrient supplies relative to atmospheric and biocycling of materials is important when assessing ecosystem response to perturbation in nutrient rich (high in basic cations) versus nutrient poor (low in basic cations) systems because the degree and rate of recovery will, in part, be related to the ability of the system to re-supply nutrients after disturbance (Trudgill 1988). Although it is the biocycling of nutrients that is important in ecosystem development, the long-term ecosystem condition can only be assessed by evaluating the potential nutrient supplies provided by weathering processes and atmospheric inputs.

Pedological studies that attempt to bridge biological (shorter time scales) and geological (longer time scales) processes by evaluating soil and landscape evolution offer another means of quantifying the effects of plants on soil weathering. For example, the annual consumption of atmospheric CO_2 by photosynthesis is nearly balanced by CO_2 released during soil and plant respiration (Raich & Schelsinger 1992). However, a small amount of the carbon cycled through the terrestrial ecosystem is not returned to the atmosphere; it is held in living biomass and soil organic matter. As stated previously, the long time-scale carbon-cycle ($\sim 10_4$ yr), over which inorganic transformations can take place, is controlled by weathering of silicate minerals. Cations released from soils as a result of weathering are charge balanced in leaching waters by HCO_3^- and CO_3^-. Terrestrial inorganic carbon is stored as dissolved inorganic carbon or pedogenic minerals in the groundwater/vadose zone. The partitioning of C and thus the weathering of mineral material within terrestrial ecosystems has been linked directly to ecological measurements such as net primary production (NPP) (Chadwick et al. 1994a).

In an attempt to fully evaluate the effects of plants on mineral weathering we summarize the quantification of mineral weathering which includes approaches such as state factor analyses, mass balance calculations, laboratory experiments and isotopic techniques. This paper provides a general overview of the current research regarding the effects of plants on soil mineral weathering. Each major set of processes is discussed and supporting research that best displays the fundamental principles is provided. We conclude with a case study from the Hawaiian Islands that takes an integrated approach to assess the effects of plants on weathering and attempts to link soil weathering to plant processes and key biological properties of the ecosystem supported by basaltic tephra.

Plant processes and mineral weathering

Production of weathering agents

The major weathering agents produced by plants include CO_2, organic acids, and ligands (Drever 1994). The amounts and chemical behavior of these weathering agents can effect the soil environment in different ways but generally provide positive feedbacks with regard to weathering potential. Soil pH is considered to be the master variable in governing many biological weathering processes and is considered a control on the rate of silicate mineral dissolution under acidic or alkaline conditions (Drever 1994). Figure 2a shows that the rate of silicate mineral dissolution increases with increasing acidity below pH ~ 4.5 and alkalinity above pH ~ 8.5 in the absence of organic ligands. It should be noted that these pH endpoints are approximate values and may vary considerably, however, they provide a reasonable range for the silicate minerals. The pH of the soil solution is determined by many competing biological and abiotic processes. Two important biological sources of acidity produced directly by plants namely, CO_2 and organic acids, can have a profound influence on soil pH, however, isolating the influence of each

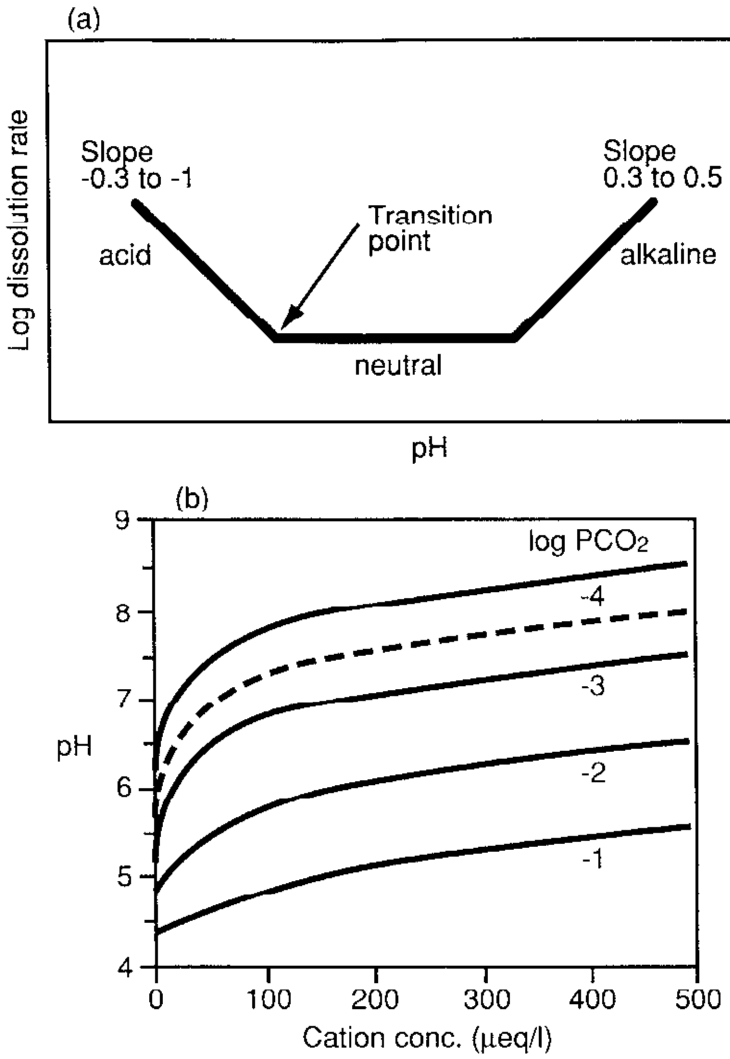

Figure 2. Relationship between pH and dissolution rate of silicate minerals (a) and pH and cation concentration (b) at varying PCO_2 (after Drever 1994).

of these biologically-produced agents may be difficult both experimentally and operationally.

The PCO_2 of the soil is generally 10 to 100 times greater than atmospheric and varies as function of climatic variables and plant and microbial activity (Amundson & Davidson 1990). The differences in atmospheric vs. soil PCO_2 levels translate into equilibrium pH of 5.65 (Log $PCO_2 = 10^{-3}$), 5.15 (Log $PCO_2 = 10^{-2}$), and 4.65 (Log $PCO_2 = 10^{-1}$) for pure water-CO_2 systems.

Figure 2b extends the pure water-CO_2 relationship to a water-mineral system depicting the relationship between PCO_2 and the concentration of cations in solution and how these variables influence pH. This figure also illustrates an important feedback between the weathering solution and the cations released in weathering reactions. As weathering proceeds, alkalinity increases as cations are released from minerals. The pH of the solution can be depressed under high PCO_2 once the system is depleted of cations as the result of extensive leaching. Extending this relationship to the soil–plant system adds another level of complexity because other organic and inorganic acids will contribute to acidity and cation release (van Breemen et al. 1983).

Organic compounds in the soil that are important to mineral weathering result from plant and microbial metabolism and are the end products of plant decomposition. Soil organic material is composed of a gradation of materials from fresh leaves to partially decomposed organic materials and various organic acids. The nature of these organic materials in natural systems is complex and difficult to characterize (Drever & Vance 1994; Schnitzer & Khan 1972). The identifiable compounds produced directly by plants encompass a range of acids including: oxalic, citric, malic, succinic, gallic, aspartic and salicylic. Some of these are derived directly from higher plant substances but in many cases the derivation is not necessarily clear (Trudgill 1988). For example, it has been found that mycorrhizal hyphae and several types of rhizosphere bacteria produce low molecular weight organic acids (Leyval & Berthelin 1991; Vandevivere et al. 1994). In greenhouse experiments Wickman and Wallander (in press) reported that concentrations of organic acids were similar in soil solution of mycorrhizal and non-mycorrhizal treatments, but reported significant differences in the concentrations of citric acid produced by two mycorrhizal associations (*S. variegatus vs P. involutus*). Some comparative studies between mycorrhizal and non-mycorrhizal treatments suggests that organic acids can reduce soil pH by 0.5–1.0 pH units (Wickman 1996). Jongmans et al. (1997) appear to provide the first direct evidence that the ectomycorrhizal mycelium are able to penetrate and colonize mineral microsites which are inaccessible to plant roots and are largely isolated from the bulk soil solution. These authors reported that fungal hyphae physically penetrate aluminosilicate minerals via strongly complexing acid exudates and create pores that may further enhance the weathering rates of minerals.

There is a real lack of clarity regarding the effects of humic acids on mineral disolution rates. Both fulvic and low molecular weight humic acids are generally considered to be important chemical weathering agents (Manely & Evans 1986; Robert & Berthelin 1986; Fox & Comerford 1990; Ugolini & Sletten 1991). Although these substances are chemically complex and may be structurally similar, their associated functional groups differ significantly. The fulvic acids generally have a greater total acidity and numbers of carboxyl groups relative to the humic acids. Both fulvic and low molecular weight humic acids are water soluble and can contribute significantly to the soil acidity by releasing protons into the soil solution upon dissociation. In addition, they contribute to mineral dissolution by acting as ligands in the processes of complexation, dissolution, and metal mobility (Schnitzer & Kodama 1977; Adams & Boyle 1979), however, this is dependent on the mineralogical composition of the parent material (Drever 1994). In contrast, Ochs (1996) demonstrated an inhibitory effect of humic acids on Al oxides at pH 4–4.5 and others (Lundström & Öhman 1990) have shown that humics from which the low molecular weight component had been removed did not accelerate feldspar dissolution. These results suggest that it may be the low molecular weight acids and not humic and fulvic acids that enhance mineral dissolution. The extent to which dissolved organic compounds contribute to acidification (by donating protons), as ligands (chelation), or both appears to be related to the degree of decomposition of the material (van Breemen et al. 1983) and their residence time in the soil environment because most are easily degraded by microorganisms (Lundström et al. 1995).

Biologically produced weathering agents are concentrated in near surface O (organic) and A (mineral) horizons or in the rhizosphere throughout the rooted portions of the soil profile. The types of weathering agents, intensities of weathering processes, and degree to which weathering products are either removed or translocated within a soil profile is related to bioclimatic and geologic conditions. There are also a host of secondary processes related to plants such as oxidation, reduction and nitrification which may also affect the chemical weathering environment (van Breemen et al. 1983). Table 1 lists the important proton donors and ligands responsible for the differential weathering of selected minerals in soil. The relative importance of inorganic versus organic acids and other ligands varies as a function of depth and results in characteristic distribution of mineral weathering within a soil profile (Boyle et al. 1974; Chadwick et al. 1994b). In some environments organic materials end up as precipitates in lower portions of the 'biological zone' and are rarely found or are found in very low concentrations in lower C horizons. In contrast, the inorganic acids and ligands are usually the major weathering agents in environments with low biological production, or in the lower portions of the soil. Biologically produced weathering agents can be directly related to plant productivity and therefore can be evaluated in terms of the types of plants involved and the environmental factors affecting their growth. Ugolini and Spaltenstein (1992) provide a theoretical assessment of the production of weathering agents in nine pedologic settings to assess regional weathering and soil formation.

Table 1. Distribution of weathering agents and important weathering reactors within a soil profile (after Ugolini & Spaltenstein 1992)

Biological Activity	Horizons	Mineral Species Weathered	Major Proton Sources	Major Ligands*	Major Weathering Reactions	Reaction Rate	Dissolution
High	O, A, E, Bh	Quarz/ Muscovite	Organic Acids	Organic	(Primary / secondary Al-silicate) + (organic acids) → (Al-organo-complex) + $(Mg,Ca,Na,K)^+$ (organic anions)$^-$ + H_4SiO_4	Very fast	congruent
Medium to Low	Bw, Bt	Feldspar	H_2CO_3	Organic/ Inorganic	(Primary / secondary Al-silicate) + $H_2CO_3 + H_2O$ → (secondary Al-silicate /hydroxide) + $(Mg,Ca,Na,K)^+ + HCO_3^-$ + H_4SiO_4	Fast	incongruent
	C1	Plagioclase	H_2CO_3	Inorganic*	(Primary / secondary Al-silicate) + $H_2CO_3 + H_2O$ → (secondary Al-silicate /hydroxide) + $(Mg,Ca,Na,K)^+ + HCO_3^-$ + H_4SiO_4	Slow	incongruent
					(Primary Fe-Al silicate) + H^+ + H_2O → (secondary Al-silicate) + (Fe-oxide / hydroxide) + H^+ + H_4SiO_4	Very Slow	incongruent
Low	C2	Biotite	Oxidation & Hydrolysis of Fe	Inorganic*	(Primary Fe-Al-silicate) + H^+ + H_2O → (secondary Al-silicate) + (Fe-oxide / hydroxide) H^+ + H_4SiO_4	Very Slow	incongruent
	C3	Amphibole	Oxidation & Hydrolysis of Fe	Inorganic*	(Primary Fe-silicate) + H^+ + H_2O → (Fe-oxide / hydroxide) + H^+ + H_4SiO_4	Extremely Slow	incongruent

*Inorganic ligands include Cl^-, SO_4^{2-}, HCO_3^-

Biocycling of cations

Biocycling of cations can provide positive and negative feedbacks in the weathering process. Theoretically, the removal of nutrients (e.g., Ca, K, Mg) from the soil solution by plant uptake and leaching could create a concentration gradient resulting in increased weathering (Trudgill 1988). The field experimentation on 'whole soils' and literature supporting this simplified model is weak. This simplified model becomes complicated because a portion of the nutrients in the soil solution are the result of atmospheric deposition and recycling of nutrients. In temperate forest ecosystems an estimated 50–90% of the annual uptake from the soil litter pool is recycled nutrients and only 10–50% of the nutrients are from atmospheric deposition and weathering (Swank & Henderson 1976; Taylor & Vebel 1991). The amounts and rates of return of nutrient cations to the soil surface through litter and roots and ultimately to the soil solution is controlled by the nature of the ecosystem and chemical make up of the plant material. For example, rates of nutrient return to the soil will vary depending on whether the plant system is aggrading (nutrient uptake > nutrient return) or degrading (nutrient return > nutrient uptake).

The most significant effect of cation cycling on weathering is related to the indirect relationship with soil pH. Changes in vegetation types can have a significant impact on the chemical nature of the soil with regard to the acidity and alkalinity that control nutrient availability and cycling (Binkley et al. 1989). Rhodes and Binkley (1996) demonstrated the influence of *Eucalyptus* and *Albizia* on soil acidification by establishing cation budgets for paired plots in Hawaii. The soil pH declined from 5.9 to 5.0 beneath plantations of *Eucalyptus saligna* and from 5.9 to 4.6 beneath *Albizia falcataria* in the top 15 cm of soil. Differences in acidification between these two species were the result of the greater depletion of cations from the exchange complex. The authors concluded that a continual supply of cations from weathering would ultimately control the pH decline and level of productivity in these plantations.

A series of controlled studies conducted at the San Dimas Experimental Forest in southern California have focussed on the influence of plants on soil properties (Quideau et al. 1996; Tice et al. 1996). These experiments, which incorporate factorial analyses (Jenny 1941), soil mass balance calculations (Chadwick et al. 1990), atmospheric inputs, plant composition, and detailed mineralogical analyses, provide an exhaustive assessment of changes in soils after 41 years of differential weathering under paired plots of scrub oak (*Quercus dumosa*) and Coulter Pine (*Pinus coulteri*). The quantities and distribution of Ca and K indicate that the degree of soil weathering is indeed different under the two vegetation types (Figure 3a). Quideau et al. (1996)

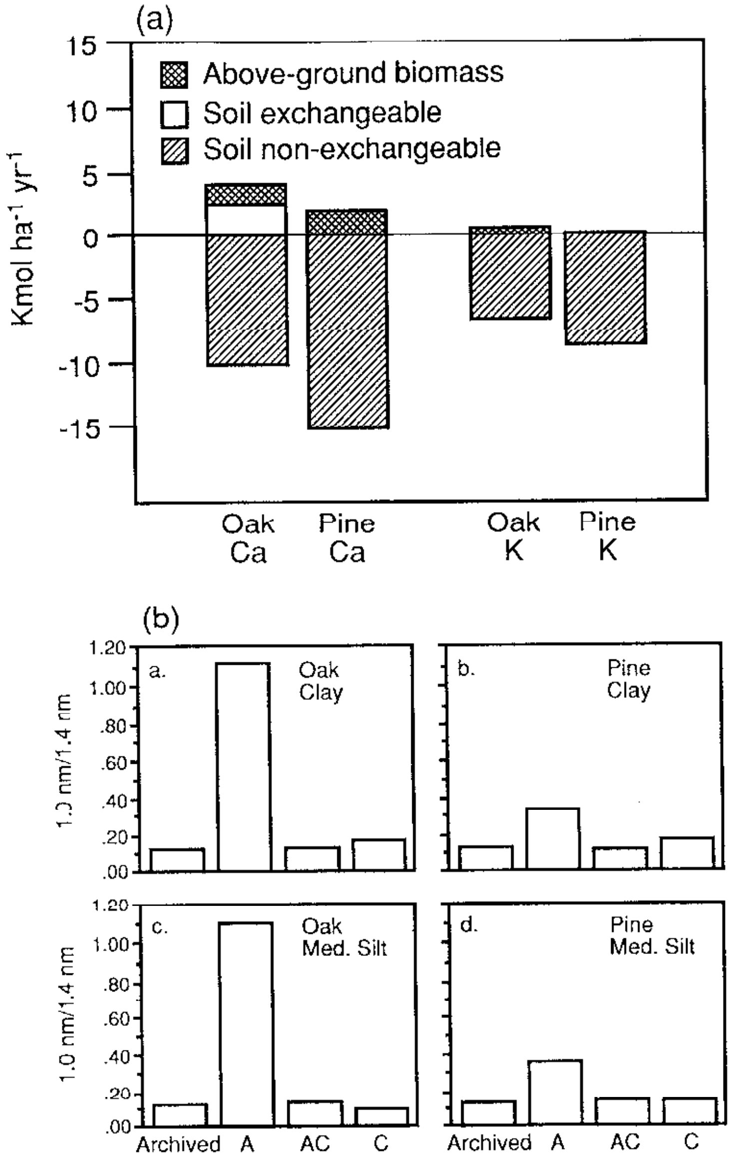

Figure 3. Mass balance of biomass Ca and K, non-exchangeable and exchangeable Ca and K in top 1 m of soils (a) adapted from Quideau et al. (1996). Peak area ratios derived from x-ray diffraction from genetic soil horizons beneath oak and pine (b) adapted from Tice et al. (1996), San Dimas Experimental Forest, California.

reported losses of nonexchangeable Ca and K and increases in exchangeable pools as a result of soil weathering under each treatment relative to archived samples. Losses and increases in the exchangeable pools were generally greater under pine and were the result of the more acidic conditions found under the pine (pH 4.9) versus oak (pH 5.8) (Ulery et al. 1995). Mineralogical characterization of the A horizon indicated that mineral alteration occurred after 41 years and varied as a function of vegetation type (Figure 3b). Tice et al. (1996) reported increases in the 1.0 nm/1.4 nm peak area ratios indicating increases in the amounts of mica relative to archived samples. The mechanism responsible for the conversion of 1.4 nm vermiculite to mica is the fixation of K by vermiculite. The pedogenic origin of the mica was believed to be the result of the higher concentration of K in oak litter relative to pine and increased rate of K biocycling by earthworms found beneath the oak and absent under pine.

Biogenic mineral production

Biogeochemical cycling of silica may significantly influence the path of soil formation by maintaining soil silica levels higher than those expected if silica could leach freely from the soil system. Once silica is solubilized and enters the biological cycle it may be removed from the soil by leaching, be involved in supergene mineral formation (i.e., kaolinite), form pedogenic opaline minerals (commonly called laminar opaline silica) or reside as biogenic opaline silica (plant opal or phytoliths). The biogenic opaline silica is easily distinguished from other forms of opaline material according to their morphological properties. Plants take up silica passively from the soil solution through the transpiration stream as monosilicic acid and deposit it in cell walls, cell luminas, and intercellular spaces near evaporating surfaces (Jones et al. 1963). Once the plant dies, this silicate material is returned to the soil upon decomposition of the plant material. These microscopic opaline particles are found in a variety of ecosystems and their abundance is related to the degree of chemical weathering (Alexandre et al. 1997), soil mineralogical composition (Dahlgren et al. 1993), plant type, and plant uptake of silica (Kelly 1989). The degree to which plants cycle silica and the quantities silica recovered as opal phytoliths have provided estimates of silica turnover in tropical environments (Lucas et al. 1993; Alexandre et al. 1994, 1997).

The significance of biogenic silica to weathering rates in soil systems is that they can vary markedly in their solubility and therefore residence time in soils. If plants are rapidly cycling nutrients, biogenic silica that is more soluble than primary silicates can be incorporated into biomass and it is likely to suppress the rate of primary silicate weathering. Others have suggested that the solubility of biogenic silica is well below that of amorphous silica gels, thus stabilizing phytolith material even in highly weathered environments (Drees et al. 1989; Trudgill 1988). In this case, phytoliths would act as a sink for Si, essentially removing it from the biological cycle. Alexandre et al. (1994) found clear indications of chemical dissolution of phytoliths and estimated that some biogenic silica in tropical rainforests of the Congo resides for no more than six months. Based on detailed studies of phytolith morphology and distribution in tropical soils Alexandre et al. (1997) developed a conceptual model that compartmentalizes silica into soil biogenic and non-biogenic components. This model further divides biogenic silica or phytoliths into labile and stable pools. They demonstrated that biogenic silica input from phytolith dissolution was twice as high as the silica release from weathering of primary silicate weathering in equatorial tropical rainforests of the Congo. They also found that approximately 7.5% of the total phytolith material was relatively less soluble then some of the non biogenic silica and that the silica release from soluble phytoliths was not sufficient to meet the demand of these tropical plants.

Hydrology of soil

Plants are a critical component in the hydrological cycle since they may influence the cycling and magnitude of net fluxes, and storage of water available for weathering in terrestrial ecosystems. The influence of plants on the cycling of water is spatially dependent and can affect the regional and local hydrologic cycle. Plants exert a major control on the regional hydrology because they increase evapotranspiration which provides water vapor to the atmosphere that is returned to the terrestrial ecosystem as rainfall. Studies of the Amazon Basin indicate that about 50% of rainfall is evapotranspired as vapor back into the atmosphere, and of which 48% falls again as rain (Salati & Vose 1984). The water that enters the soil can go through several precipitation-evapotranspiration cycles before it leaves the terrestrial system (Stallard & Edmond 1981; Salati & Vose 1984). As a result, water entering these tropical soils available for weathering processes may have been cycled through soil several times before entering the ocean (Drever 1994).

At local scales plants exert a control on the moisture content of soils by lowering the impact of rainfall, reducing overland flow, decreasing soil leaching, and increasing infiltration rates (Bach et al. 1986). Plants also remove large quantities of water stored within the soil during transpiration and effectively transfer water back to the atmosphere that has been stored deep within the soil profile (Schlesinger 1991). Evidence of the influence of plants on soil water content is based on studies where the removal of vegetation causes an increase in soil moisture content (Ting & Chang 1985; Schlesinger et al. 1987) or where there are reported increases in volume and chemical constituents of stream flow (Bormann & Likens 1979; Dahlgren & Driscoll 1994). The relative amounts and pathways of water loss vary considerably with climate and vegetation type. For example most water loss in tropical rain forests due to evaporation ranges from 10 to 25% of the total water budget whereas the remaining 90 to 75% is lost through transpiration and surface runoff (Salati & Vose 1984; Shuttleworth 1988). In temperate ecosystems the difference between forests and grasslands is evident. Waring et al. (1981) reported estimates of water loss due to evaporation of 13% of the total water budget whereas transpiration and runoff losses accounted for 32 and 55% respectively. In temperate systems dominated by grasses evaporation losses range from 35 to 55% of the total and transpiration losses ranged from 65 to 45% (Trlica & Biondini 1990). Studies of the specific influences of vegetation type on the soil hydrologic regime have been directed toward the effects of deforestation on soil moisture. Deforestation affects albedo, interception by the canopy and surface roughness as well as the radiation reaching the ground; all of these have significant impacts on the soil water balance. Most of the change in soil moisture is attributed to changing albedo which can increase as much as 150 times immediately after deforestation (Changmon & Semonin 1979). The increased solar radiation at the soil surface changes surface temperatures and other microclimatologcial parameters which may influence the soil hydrologic regime and perhaps the residence time of water in soils.

Quantification of mineral weathering

The quantification of the effects of plants in soil mineral weathering is generally weak due to the difficulties associated with studying weathering processes in soil-vegetation systems. The methods selected to estimate weathering rates involve both field and laboratory procedures, each of which can yield very different results. Quantification of chemical weathering and the degree to which these processes can be detected across different temporal scales is primarily based on: (1) studies of mineral alteration (thermodynamic and kinetic effects), and (2) estimates of the loss of basic cations from minerals over some interval (cation denudation). These types of characterization data are usually embedded in laboratory or field-based research designed to isolate how the amounts, different types (e.g., angiosperms vs. gymnosperms), or chemical nature of plants influence weathering.

Laboratory experiments (or batch experiments) provide important information regarding the weathering mechanisms rather than quantitatively assessing rates (Boyle et al. 1974). The operational conditions established in the laboratory are quite different from actual field conditions with regard to open vs. closed systems (removal of weathering products), solution/solid ratios, flow homogeneity, and changes in the soil chemical environment during weathering (Wickman 1996). Weathering rates determined in the laboratory are generally orders of magnitude greater than field predictions. The discrepancies can be attributed to several factors, namely, surface area differences between standardized minerals versus heterogenous mineral mixtures collected from the field, formation of secondary precipitates, macropore flow, and formation of weathering rinds, each of which would decrease weathering rate calculations (White et al. 1996).

Mass balance approaches are often utilized to determine weathering rates and vary based on the scientific questions of interest. Differences in the utilization of cation denudation rates can result in large variations in calculated mineral weathering rates. In general, this approach requires accurate evaluation of inputs and outputs to the system being studied. Fundamental differences regarding the exclusion or inclusion of soil or vegetative components are evident. Velbel (1995), in a summary of four watersheds, demonstrated that mass balance determinations that did not account for biomass storage components could differ by as much as a factor of four. Other differences in determinations of weathering rates involve assumptions regarding specific soil properties. Assumptions regarding the steady-state vs. non-steady conditions of the exchangeable cation pool may yield very different rates. Under the assumptions of a steady state condition, Cl^- is considered to be the conservative ion in all of the mass balance calculations. Knowledge of soil chemistry is not necessary and the weathering rate is simply the difference between inputs and outputs within a monitored watershed. When non-steady-state conditions are assumed, changes in the store of base cations (which are from weathering and exchange reactions) are made relative to Si (which is assumed to be a product of weathering). This method requires knowledge of both soil and water chemistry and total base cation deposition (Paces 1986; Bain et al. 1994).

Soil mass balance determinations require more detailed information regarding the mineralogical and chemical alteration of the soil profile relative to parent material (Brimhall et al. 1992; Bain et al. 1993). Accurate calculations of chemical mass gains and losses due to mineral dissolution and leaching are possible by comparing elemental concentrations, volumes, and bulk density in soil horizons with those in a well-characterized parent material (Chadwick et al. 1990). To correct for material losses an immobile element such as Zr, Ti, or quartz can be used for calibrating the mass balance. This approach assumes uniformity of parent material and does not require knowledge of water chemistry as all assessments are made relative to unweathered material. However, atmospheric deposition to the system and variations in soil age determinations could influence calculated weathering rates (Brimhall et al. 1992). Weathering rates are essentially averaged over long time periods (10 ky and greater) and it is generally acknowledged that instantaneous rates (measured in the lab) would be very different.

Isotopic techniques offer another means of quantifying weathering rates. Sr isotopes ($^{87}Sr/^{86}Sr$ ratios) can be used as proxies for Ca as their chemical behavior is very similar (Graustein 1989). The primary sources of cation nutrients (such as Ca, Mg) to the soil ecosystem are the products of chemical weathering and atmospheric deposition. The $^{87}Sr/^{86}Sr$ ratio of chemical weathering products carries the isotopic signature of the parent material and can be used as an indicator of provenance (Dasch 1969; Brass 1975). Living plants, soil organic matter, and other organic materials carry the isotopic signature of an ecosystem's nutrient reservoir. If the *in situ* and external sources of Sr to the soil have distinct Sr isotopic signatures, the $^{87}Sr/^{86}Sr$ ratio can be used to track the movement and provenance of Sr through the ecosystem (Graustein 1989). Once the endpoints have been established (weathering versus atmospheric inputs) weathering rates can be determined from runoff water by evaluating the Sr added to precipitation as it moves through the soil. The added Sr from the soil exchange sites provides an estimate of the current weathering rate. It is difficult in some cases to get a reliable estimate of the Sr released by weathering as there is considerable variability in the Sr concentrations of different minerals within rocks as well as differences in weathering susceptibility. In order to fully utilize this method it may be necessary to conduct detailed Sr analyses of mineral separates and incorporate the dissolution kinetics of each mineral (Wickman 1996). In order to effectively use Sr as a geochemical proxy of Ca in determining weathering rates, the relative concentrations of Sr and Ca and inputs and outputs to the system must be known.

Many field- and laboratory-based experiments utilize some degree of factorial analyses where the underlying assumption is that soil weathering is regulated by the driving variables climate, organisms, parent material, relief, and time (Jenny 1941). These factors are rarely independent from one another, but scientists can utilize this approach by isolating one variable for investigation (plants for example) and minimizing differences among other variables. The complexities associated with this quantitative approach for isolating the influence of plants on soil processes are recently discussed by van Breemen (1993) and Wilding and Kelly (1993). The factorial approach is very useful for conducting mineralogical, and isotopic, and mass balance determinations at the scale of the soil horizon, pedon, landscape and watershed.

Case study: Soil weathering along a tropical bioclimatic gradient

To test the validity of conceptual models regarding weathering in soils we designed a study that integrates factorial analysis, soil mass balance calculations and isotopic technique, to evaluate the influence of rainfall, plant type,

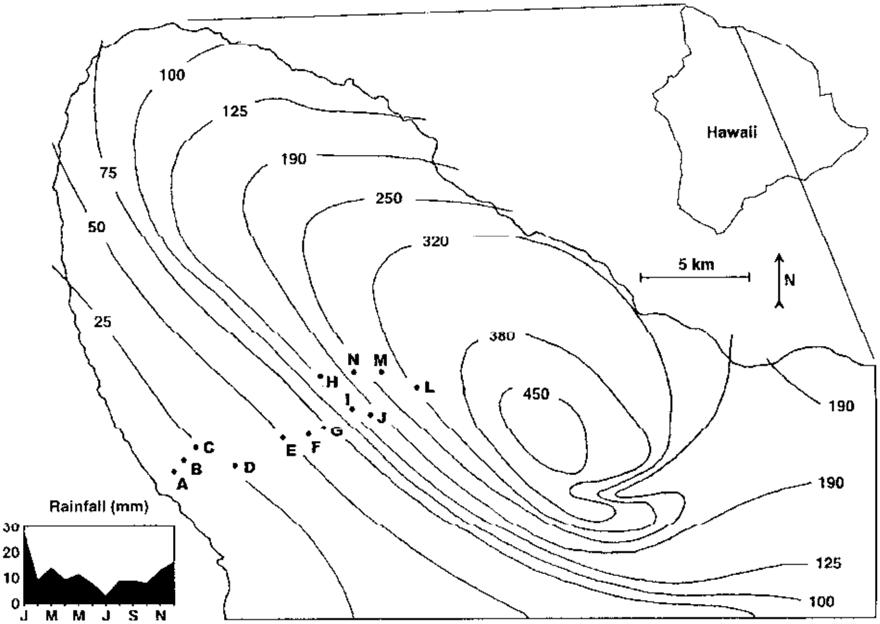

Figure 4. Site locations along bioclimatic transect, Kohala, Peninsula, Hawaii, USA.

and production on the chemical, biological and mineralogical properties of soils (Hendricks et al. 1993; Kelly et al. 1993). Specifically, we attempt to assess the how the role of plants in soil weathering changes across an environmental gradient (increasing rainfall and plant production) by evaluating long term variations in soil chemical and mineralogical properties. We use soil organic C as a proxy for relative plant production over time because it is generally the best single indicator of ecosystem status and long term net primary production (Burke et al. 1991). Clearly there are many variables involved in assessing organic carbon levels in soils, however, our assessment is over millennial time scales and incorporates variations due to regional climate over time. Finally, we compare soil weathering between a native forest and pasture (forest cleared approximately 110 years ago) and attempt to assess the impacts of changing vegetation type on the chemical nature and mineralogical composition of soils.

Experimental design and methods

Utilizing a factorial approach we established a bioclimatic sequence by selecting sites along a precipitation gradient of 18 to 350 cm MAP on the Kohala Peninsula, Hawaii (Figure 4). Variations in other soil forming factors (topography, parent material composition and age) across the gradient were minimized (Jenny 1941, 1980). The mineralogical composition and age (~170 ka) of the parent material (basalt/tephra mixture) was similar across the gradient and soils were sampled on well-defined constructional topographic surfaces of the shield volcanoes. The Hawaii shield volcanoes are composed of highly weatherable lava that ranges from theolites rich in olivine and clinopyroxene to hawaiites rich in plagioclase (Spengler & Garcia 1988). The elemental and mineralogical nature of the tephra additions to soils has been assessed by sampling nearby cinder cones. Across much of the area the natural forest vegetation has been altered and exotic grasses (Buffel, Keawe) span the entire precipitation gradient. The historical and pre-historical deforestation of the Kohala Peninsula has resulted in a pasture-forest mosaic and allows for the assessment soil weathering as a function of plant production (similar plants across entire precipitation gradient) and plant type (grasses vs. trees) within the same precipitation zone.

Soils were sampled by genetic horizon to a depth of 2 meters and samples were subjected to routine chemical and physical characterization, including particle size, organic carbon, pH, % base saturation, exchange acidity, exchangeable bases, bulk density, and total elemental analyses (Soil Survey Staff 1994). Mineral identification of soil samples was accomplished using x-ray diffraction techniques, petrography and sequential selective dissolution which included: (1) removal of organic-mineral complexes with sodium pyrophosphate (Wada 1989), (2) removal of non-crystalline materials (McKeague & Day 1966), (3) removal of crystalline Fe-oxides by Na-dithionite and Na-citrate (Holmgren 1967), (4) removal of poorly crystalline silicates (Jackson et al. 1986), (5) removal of kaolin by heating. The remaining components were back calculated from total dissolution residue (Alexiades & Jackson 1966). To help assess the degree of biological alteration due to deforestation soil organic carbon samples were subjected to stable carbon isotope analysis ($^{13}C/^{12}C$ ratios) (Bender 1968; Cerri et al. 1991).

To quantify C sequestration over the bioclimatic gradient we made direct measurement of the organic C stored in all soil profiles, carbonate C stored in arid soil profiles, and carbon consumed during silicate weathering. The details of the methods and equations used for these calculations are outlined by Chadwick et al. (1994a). Briefly, the C consumed during weathering is based on mass balance relationships among soil chemical composition, bulk density, and volume change in relation to soil parent material (Chadwick et al. 1990; Merritts et al. 1992). We assume that cation leaching controls the quantity of bicarbonate removed from each soil profile. The mass loss of each cation is converted to moles of positive charge which is balanced by the negative charge from bicarbonate.

Weathering potential changes related to plant production

The variations in soil organic C, percent base saturation, pH, and effective CEC are presented as weighted averages for the top 1 m of soil (Figure 5). Because the current vegetation type is constant across the rainfall gradient we use soil organic C as a proxy for long term plant production. The relative changes in soil organic C indicate substantial increases in plant productivity as a function of increasing precipitation (Figure 5a). Along with these increases in organic C there is an observed decline in % base saturation and pH at approximately 150 cm precipitation (Figures 5b,c). The effective cation exchange capacity (CEC) increases at the drier end of the gradient to about 150 cm and then declines sharply to less than 5 meq $100g^{-1}$ decline at 220 cm precipitation (Figure 5d). The change in CEC is the result of greater accumulation of organic carbon in higher rainfall zones and changes in the mineralogical composition of the clay minerals which ranges from kaolinite/smectite/gibbsite at sites with less than 150 cm precipitation to kaolinite and oxides of Fe at higher precipitation zones. The dramatic change in % base saturation is due to the corresponding losses of Ca, Mg and Na and decreasing CEC. An indirect influence of plants on soil weathering and the chemical nature of the soils is evident in the mineralogical composition of the clay size fraction of the soils. The large increase in organic carbon and corresponding decline in soil pH results in the suppression of gibbsite formation in soils forming in rainfall zones above 150 cm. At an annual rainfall of 150 cm the pH of the soil system drops below ~4.9 and it is suggested that Al-humus complexes form preferentially to Al-OH complexes (Shoji & Fujiwara 1984). The higher amounts of organic C at sites with greater than 150 cm precipitation appear to complex a significant amounts of soluble Al and depress the formation of gibbsite which is thermodynamically stable under these chemical conditions (Lindsay & Walthall 1996).

Plant mitigated transfers of atmospheric CO_2 into weathering processes (lost as bicarbonate) and organic C storage were estimated utilizing soil mass balance calculations (Chadwick et al. 1994a). The total organic C stored in the soil increases as a function of rainfall ranging from 2.0 kg C m^{-2} at 18 cm MAP to 46.0 kg C m^{-2} at 350 cm MAP (Figure 6a). Along the same precipitation gradient the rate of organic C accumulation also increases from 0.02 g C m^{-2} yr^{-1} to 0.27 g C m^{-2} yr^{-1} (Figure 6b). The cumulative amount of atmospheric carbon dioxide transferred by plants to bicarbonate and lost through leaching increases in a curvilinear fashion and is approximately 7 times greater at 350 cm precipitation ranging from 11.0 kg C m^{-2} in areas of low rainfall to 76.0 kg C m^{-2} in high rainfall (Figure 7a). Across the same precipitation range the long term C fluxes due to weathering is 5.7 times greater under high rainfall increasing from 0.08 to 0.46 g C m^{-2} yr^{-1}

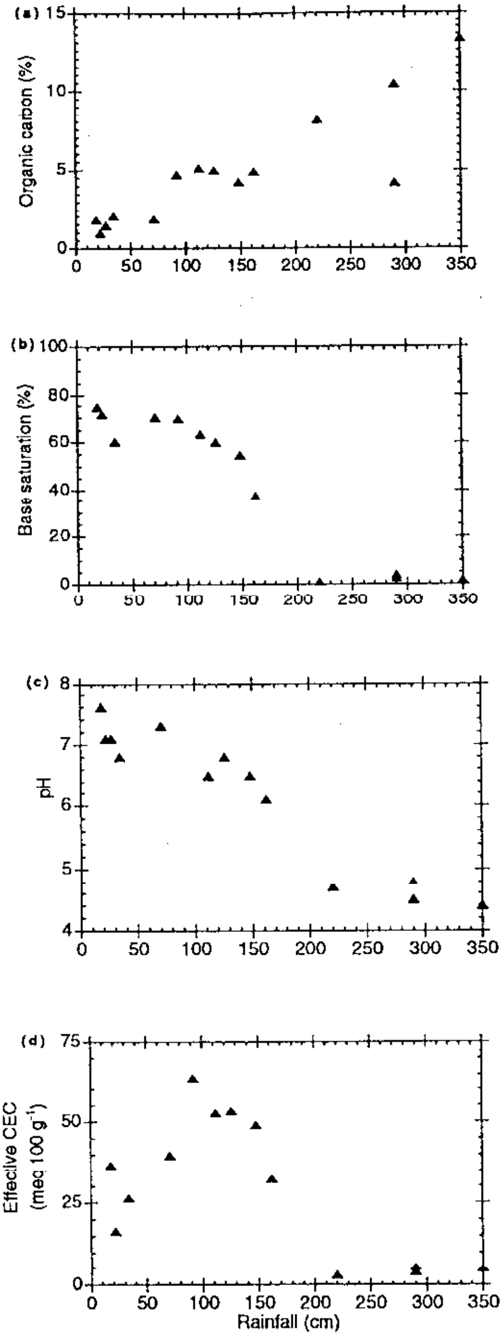

Figure 5. Depth weighted averages of selected soil properties in the top 1 meter of soil as a function of increasing rainfall, Kohala Peninsula, Hawaii, USA. (a) Soil organic C content (wt.%); (b) percent base saturation; (c) soil pH, (d) effective cation exchange capacity (CEC).

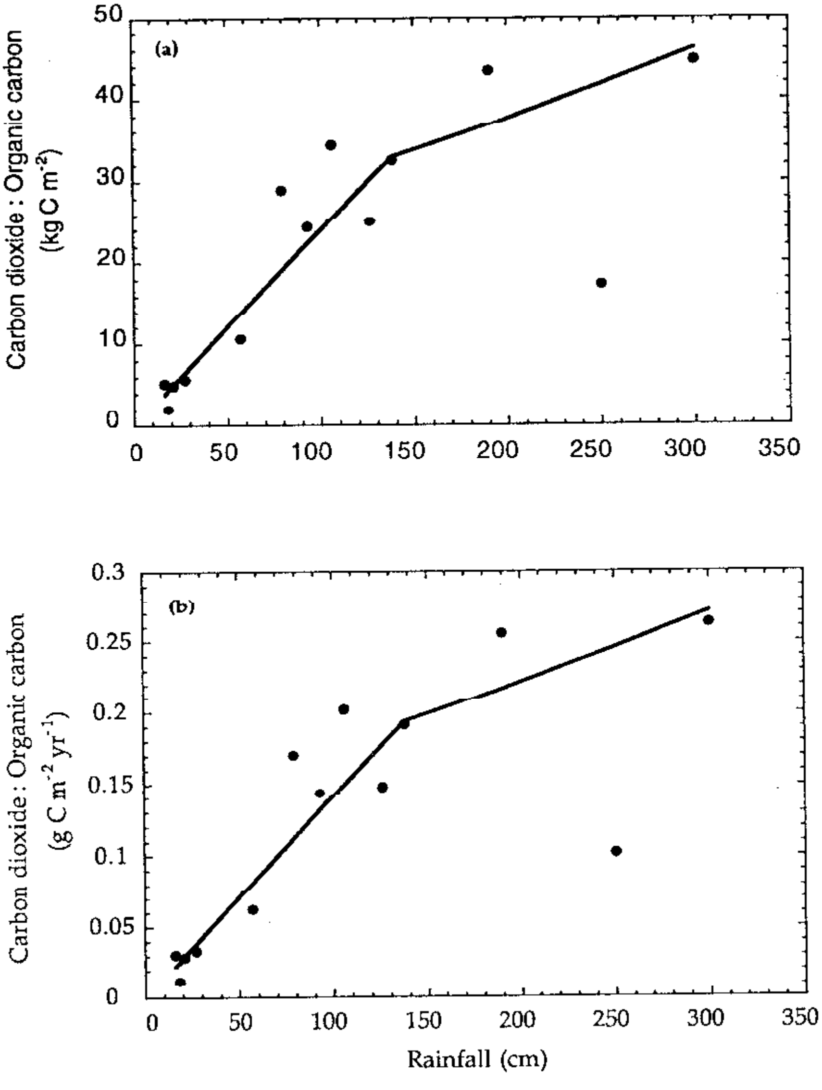

Figure 6. The transfer of CO_2 to organic carbon (a) cumulative amounts and (b) fluxes accumulated in soils as a function of increasing rainfall.

(Figure 7b). These data indicate that the total C sequestration and the rate of C consumed by weathering are greater with increasing rainfall and plant production. When comparisons are made from studies conducted with similar mean annual precipitation on similar age soils these data indicate that both the storage and fluxes of organic C are 2.5 to 3 times lower than values reported for temperate regions while cumulative C consumption quantities

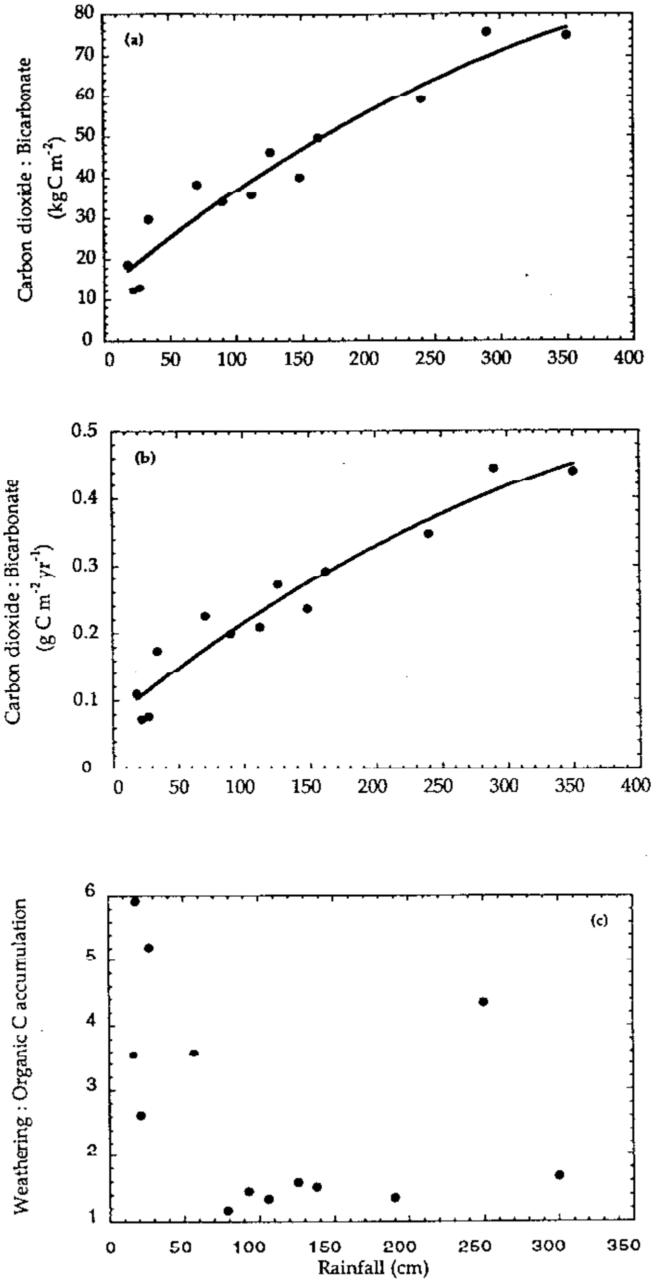

Figure 7. The cumulative amount (a) and flux (b) of bicarbonate leached soils as a function of increasing precipitation. Ratio (c) of rates of carbon consumed by weathering vs. C accumulation as organic carbon along bioclimatic gradient.

due to weathering processes are 2.2 to 4.3 times greater than reported in temperate regions (Chadwick et al. 1994a). The ratio of C consumption rates by weathering processes to soil organic C accumulation rate is greater in areas of lower plant production and decreases dramatically with increasing rainfall between 90 and 100 cm (Figure 7c). This comparison of sequestration rates indicate that organic C accumulation becomes a more important sink for C relative to weathering processes in higher rainfall areas.

Due to the mineral depletion and increased atmospheric deposition (Capo et al., in press) in higher precipitation zones it is unlikely that plants contribute significantly to weathering processes with regard to the biocycling of cations or as producers of bicarbonate ligands. They do appear to provide organic acids that play a major role in generating soil acidity and the complexation of Al that inhibits gibbsite formation in areas of higher rainfall. In areas of lower rainfall and productivity weathering processes are still the primary source of nutrients (Capo et al., in press). The bicarbonate C consumed by weathering becomes a larger component of the total C (biomass, soil organic C and bicarbonate) flux under arid conditions and is likely to be the primary plant-produced weathering agent.

Weathering potential changes resulting from deforestation

In evaluating the influence of deforestation on soil properties in Hawaii we have noted changes in the nature and distribution of soil chemical components in paired forest and pasture soils at approximately 300 cm precipitation. The pasture site was converted from native rainforest 110 years ago using methods which did not burn the residual vegetation. To quantify the degree of biological alteration resulting from deforestation we utilized stable C isotopes to evaluate organic matter changes resulting from deforestation (Cerri et al. 1991; Townsend et al. 1995). The comparison of ^{13}C values of soils formed beneath pasture vs. forest (Figure 8) indicates that almost 100% of the soil organic C below 75 cm depth is from the original forest vegetation where organic C near the surface appears to be altered chemically as a result of deforestation. Approximately 60–70% of the original organic C remains in the surface layers although an average organic C loss of 40% is the result of the original deforestation.

Total amounts of soil chemical components can have large increases or decreases after deforestation. Comparison of total sizes of several pools in the top one meter of soil at both sites for selected chemical attributes is shown in Table 2 and Figures 9 and 10. The depth distribution of organic C for the forest and pasture (Figure 9a) are similar below approximately 60 cm, but diverge above, so that the A horizon of the pasture soil contains only 3.8% organic C compared to 22.9% in the soil beneath forest vegetation. Base cations are

Table 2. Total amounts in the top one meter of mineral soil (kg m^{-2})

Pool	Forest	Pasture	Pasture Gain or Loss	
Organic C	101.5	39.9	−61.6	(−60.7%)
SiO_2	199.3	176.3	−23.0	(−11.5%)
Al_2O_3	110.1	32.3	−77.8	(−70.7%)
Fe_2O_3	134.8	249.0	114.1	(84.6%)
Base Cations	14.5	20.7	6.20	(42.8%)

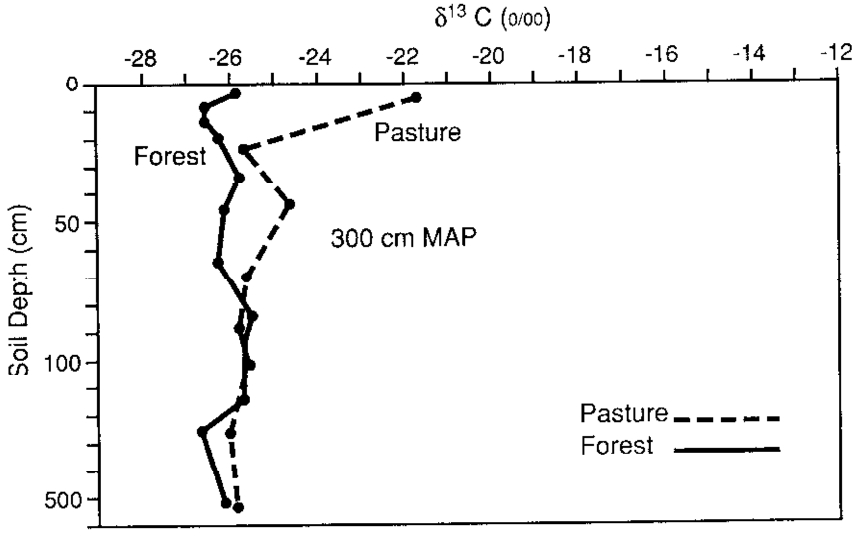

Figure 8. Changes in the δ ^{13}C values of soil organic carbon 85 years after conversion of forest to pasture Kohala Peninsula, Hawaii, USA.

retained in the soil beneath pasture relative to the original forest, an increase of 42.8% (Figure 9b, Table 2). The large cation pool size may reflect more rapid cycling of cations in soil by pasture grasses relative to forest vegetation. The pH of the O horizon in the forest is much more acidic than the mineral A horizon in the soil beneath the forest and pasture vegetation, however, soil pH in the upper 50 cm of mineral soil is similar for both sites (Figure 9c). Soil pH below 50 cm is more acidic in the pasture and is likely the result of organic acid production at depth. In both soils, the sum of base cations correlates positively with organic C and negatively with pH.

Organic C, SiO_2, and Al_2O_3 pools have decreased significantly after deforestation, while Fe_2O_3 and the sum of base cations pools have increased. The decreases in organic C, SiO_2, and Al_2O_3 may be accounted for by their removal with aboveground biomass during deforestation, and subsequent

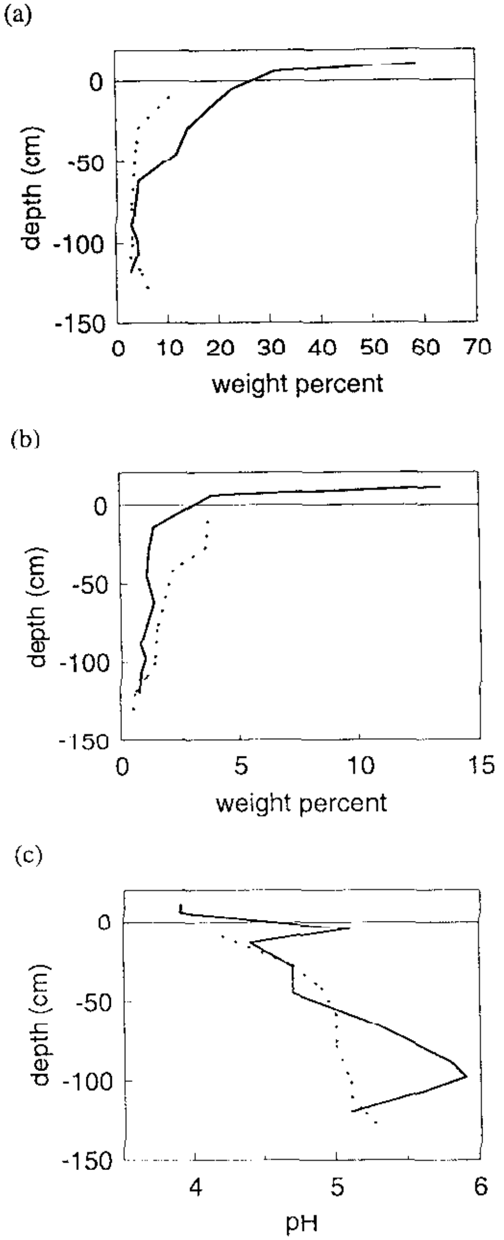

Figure 9. Depth distributions of organic C, base saturation, base cations, and pH for a forest and pasture site pair. The lines represent forest (solid) and pasture (dotted). Data includes buried horizons and Oa and Oe horizons, (a) Organic C, (b) Base cations, (c) pH.

leaching. Dahlgren and Driscoll (1994) observed greatly increased acidity in the five years following whole tree removal which mobilized and leached Si and Al. Parfitt et al. (1997) documented decreases in organic C in pasture soil 130 years after deforestation of 47.4%.

The changes in the compartmentalization of silica when forests are converted to pasture grasses are substantial (Figure 10a and 10b). The total Si content of the soils beneath the pasture and forests is similar (Figure 10a and Table 2) but the ratio of acid oxalate-extractable Si to total Si is much higher in the forest soil (Figure 10b). Based on these data it appears that the forest ecosystem maintains greater amounts of more soluble silica than the pasture. However, total Si amounts correlate strongly with oxalate extractable Si in the pasture soil, but have no correlation in the forest soil suggesting that pasture soils have a single Si pool, while the forest has two pools. Based on this we have hypothesized that the grasses, which produce more phytolith per unit weight than trees (Piperno 1989), have stabilized a greater proportion of the soil silica by producing phytoliths. This biological transformation of the more soluble silica to a less soluble form could have a dramatic effect on the weathering of the soils and the total biogeochemical Si cycle of these ecosystems. The relative degree of Si cycling may be reflected in the correlation of organic C with oxalate Si. In the forest soil, the inverse relationship of organic C with oxalate Si and the oxalate to total Si ratio suggests that increased biogenic cycling of Si in more biologically-active horizons leaves less available Si the soil. The pasture soil shows a weaker relationship, suggesting either a lower net rate of cycling, or lesser ability of grasses to mobilize a large fraction of the total Si.

Soil mineralogy for non-crystalline, free sesquioxide, and poorly crystalline fractions is shown in Figure 11. In terms of the total pedon, the fraction of the forest soil that is non-crystalline is much greater than in the pasture soil (Figure 11a). Conversely, the fraction of the pasture soil composed of free sesquioxides is much greater than in the forest soil (Figure 11b). The pedon total and the depth distribution of the poorly-crystalline fraction is similar for both soils (Figure 11c). The depth-distributions of the non crystalline fraction resembles the distributions of Al_2O_3 (Figure 10c) in pattern and relative magnitude. Likewise, the distribution of the poorly-crystalline fraction resembles the distributions for SiO_2 (see Figure 10a). These observations suggest that Al oxides dominante the non-crystalline fraction, and silica dominates the poorly-crystalline fraction.

The change from forest to pasture vegetation alters the biological, chemical and mineralogical properties of the soil. The retention of cations in the soil beneath the pasture vegetation relative to the forest may be the result of the direct influence of grasses on the cycling of cations. An alternative explanation

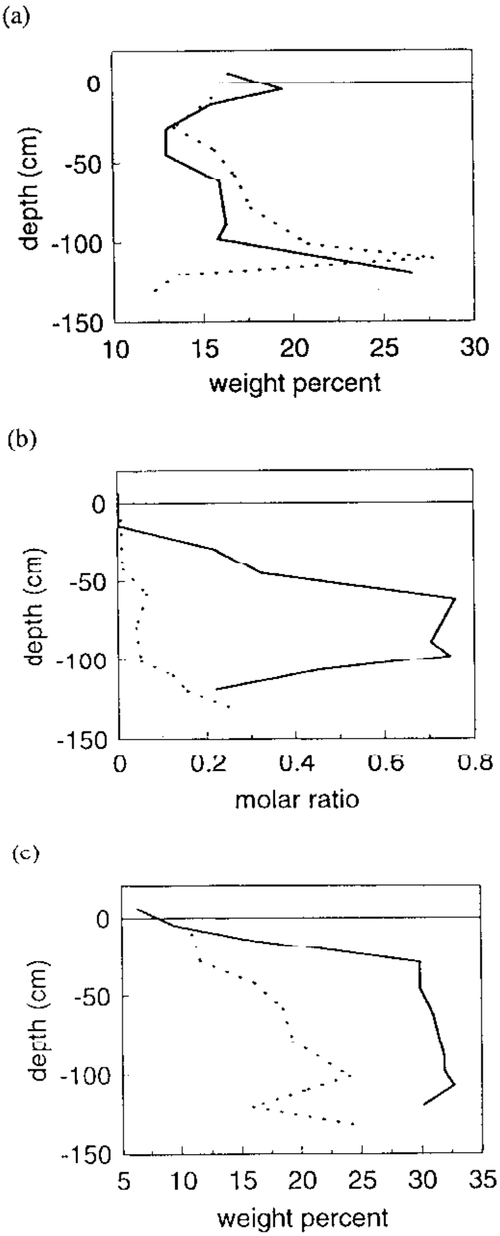

Figure 10. Depth distribution of Si and Al for a forest and pasture site pair. The lines represent forest (solid) and pasture (dotted). Data includes buried horizons and Oe horizon. (a) Total SiO_2, (b) molar ratio of acid oxalate extractable Si to total Si, (c) total Al_2O_3.

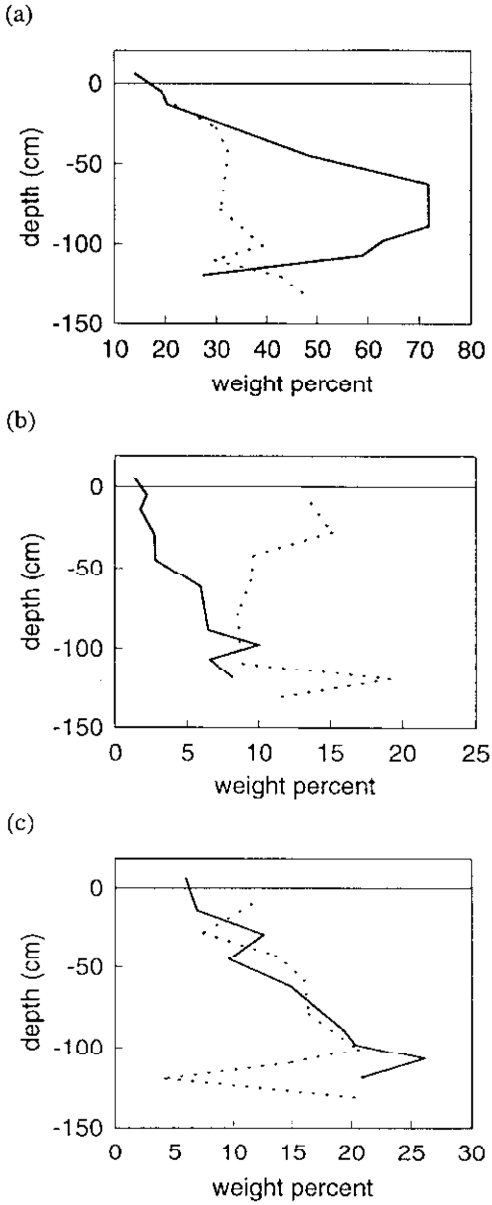

Figure 11. Depth distributions of total non crystalline, total free sesquioxide, and total poorly crystalline fractions for a forest and pasture site pair. The lines represent forest (solid) and pasture (dotted). Data includes buried and Oe horizon. Each fraction is the sum of Si, Al, and Fe extracts in weight percent. (a) Total non-crystalline, (b) total free sesquioxide, (c) total poorly crystalline.

could be that the hydrologic regime of the soil has been altered by deforestation and perhaps reduced leaching has occurred under the pasture vegetation relative to the forest. The forest soil appears to have two silica pools, and the pasture one pool, reflecting a greater proportion of plant-available silica under the forest and a greater proportion of phytolith-stabilized silica under the pasture. The retention of Al in the soil under forested conditions relative to the soils beneath pasture is likely the result of its complexation by organic matter at low pH and rapid losses of Al immediately after deforestation.

Summary

Plants are important in the transfer of atmospheric carbon dioxide into the mineral weathering cycle and the relative importance could be related to ecosystem properties such as NPP. However, the relationship between NPP and weathering appears to be conditioned by the climatic and geologic setting. In regions where primary mineral supplies are depleted, plants are more likely to play a greater role in biocycling of cations and production of organic acids. In areas subjected to deforestation, pasture grasses appear to have a greater capacity to retain basic cations and to transfer silica into more stable forms that may alter weathering processes and the biogeochemical silica cycle. This Si sink in soils may provide a negative feedback with regard to weathering potential. The affect of plants on soil hydrologic conditions is well documented but poorly quantified with regard to soil weathering potential. In general, the specific role of plants in weathering processes are quite variable and is dependent on climatic and geologic conditions of the region.

Several fundamental problems have limited the reliability and accuracy of making direct links between weathering potential and plants. Among the most limiting have been: (1) lack of studies in climatically diverse settings that evaluate the changes in long-term soil nutrient content and soil mass changes (denudation vs. aggradation), (2) reliable means of linking nutrient content of biological components to provenance of nutrients (atmospheric vs. weathering inputs), (3) a quantitative understanding of the relationship between vegetation and local and regional hydrologic cycles, and (4) lack of information regarding the relationship among long term productivity (NPP), internal cycling of nutrients and soil mineral weathering. The advent of interdisciplinary ecosystem studies and the development of new stable isotope techniques and mass balance models promise an evolution, if not a revolution, in quantifying the contribution of plants to mineral weathering and a further quantification of regional biogeochemical cycles. These techniques, in addition to more traditional approaches such as soil micromorphology, total chemical and mineralogical analyses, and watershed studies may help us assess the critical nutrient thresholds in ecosystems and quantify feedbacks between plants and the weathering processes.

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