THE BIOGEOCHEMISTRY OF PHOSPHORUS CYCLING AND PHOSPHORUS AVAILABILITY ALONG A DESERT SOIL CHRONOSEQUENCE[1]

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Abstract. The biogeochemistry of the weathering, landscape movements, and chemical transformations of phosphorus and its availability to plants were examined in a chronosequence of soils developed from quartz monzonite alluvium in southern New Mexico. Total P in the soil profile decreased with increasing soil age and was removed from the ecosystem as readily as the most easily leachable base cations. Although Ca-bound forms of P decreased with increasing soil age, Ca-P remained the single largest fraction of total P in all soils. In contrast, Fe- and Al-bound P was a very small percent of total P in all soils. There was little evidence for the stabilization of P by soil organic matter within this ecosystem; both soil organic P and microbial P represented very small pools of total soil P. Phosphorus availability, measured by in situ resin bags, was not well correlated with soil age or total soil P, and P concentrations in shrub tissues did not reflect changes in forms or total amounts of soil P. The biogeochemical cycle of P in this system differs sharply from that in a more mesic, forested system, where fixation by iron and aluminum oxides and biologic activity play more dominant roles in the conservation of P within the ecosystem.

Key words: biogeochemistry; chronosequence; desert ecosystem; nutrient cycling; phosphorus; weathering.

INTRODUCTION

Phosphorus is a major element in soil organic matter whose primary source is the weathering of minerals in parent rock material. As there is no gaseous component to the phosphorus cycle, losses of phosphorus from a system can be replenished only by the release of phosphorus from primary minerals such as apatite. Thus phosphorus cycles through ecosystems on a geologic time scale, and the cycle is dominated by geochemical factors.

Several studies have shown that phosphorus can serve as a useful indicator of pedogenic processes. Smeck (1973) concluded that changes in chemical forms and the distribution of phosphorus within soil profiles were functions of the degree of weathering and soil development within the landscape. Walker and Syers (1976), working on a soil chronosequence in New Zealand, proposed a general model for changes in the forms and amounts of phosphorus with time. As a result of weathering, phosphorus from primary apatite minerals is released into the soil solution where it may be leached, taken up by plants and microorganisms, or transformed into secondary mineral forms. As soils weather, pH declines, cations are lost, aluminum and iron oxyhydroxides are generated, and phosphorus is gradually transformed from primary Ca-phosphate minerals to

secondary Fe- and Al-phosphate minerals. Phosphorus availability in the soil solution is then controlled by the solubility of calcium, aluminum, and iron phosphates (Lindsay and Moreno 1960, Smeck 1973, Marion and Babcock 1977). Critical to this model is the assertion that decreasing pH is the driving force in the conversion of primary phosphate minerals to secondary forms (Smeck 1985). As vegetation develops, the pool of soil organic P increases until the weathering release of apatite phosphorus is less than the loss of phosphorus due to transformations to secondary minerals and to leaching.

Arid-land soils show several distinctive differences from soils of more humid regions, and some of these differences could cause the geochemical transformations and availability of phosphorus to differ fundamentally between arid and humid soils. A characteristic feature of soils in the southwestern United States, as well as many soils of arid regions worldwide, is the presence of high concentrations of precipitated carbonates (Dregne 1976, Schlesinger 1982). The distribution and physiology of plants in relation to the presence of these pedogenic carbonates, and to the presence of caliche horizons in particular, have been well documented (Shreve and Mallery 1933, Cunningham and Burk 1973, Hallmark and Allen 1975). Less well documented, however, is the effect of these carbonates on nutrient cycling, particularly phosphorus cycling, in arid soils.

Soils of humid or tropical forests, rich in free iron and aluminum hydroxides and sesquioxides, tend to
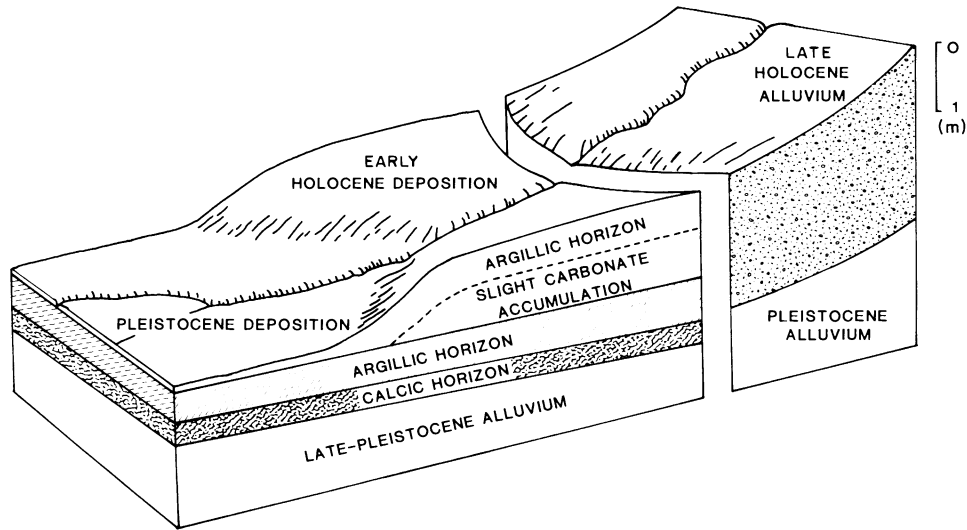
Fig. 1. A generalized model of soil deposition and soil horizon formation on piedmont slopes in an arid environment (adapted from Gile 1975).

have high phosphorus-fixing capacities, rendering phosphorus very immobile and often quite unavailable for plant uptake (Laverdiere 1982, Wood et al. 1984). In alkaline ecosystems where iron and aluminum phosphates are more soluble, sorption and precipitation reactions with pedogenic calcium carbonate may stabilize soil phosphorus and lower free phosphorus in the soil solution (Tiessen et al. 1983, 1984). Carbonates can potentially control phosphorus levels in soil solutions through ion pairing with calcium, physical sorption, and the precipitation of calcium phosphate minerals (Griffin and Jurinak 1973, Holford and Mattingly 1975, Marion and Babcock 1977).

Evidence from soil chronosequences suggests that the phosphorus content of parent material and the amount of phosphorus remaining in weathered soils are major factors governing both net primary production and the accumulation of nitrogen and sulfur within ecosystems (Walker and Adams 1958, 1959, Syers and Walker 1969, Williams and Walker 1969). Cole and Heil (1981) also emphasized the importance of phosphorus in controlling aspects of organic matter production and nitrogen cycling. Certainly nitrogen fixation, especially in early stages of primary succession, can be shown to be dependent on phosphorus availability (Griffith 1978). Similarly, carbon and nitrogen mineralization rates have been shown to be related to phosphorus supply in a variety of ecosystems (Purchase 1974, Munevar and Wollum 1977, Ross and Bridger 1978, Pastor et al. 1984).

Few studies of nutrient cycling in ecosystems link the geochemical cycles, pedogenesis, and the subsequent plant availability of nutrients. This study examines the weathering, chemical transformations, availability, and movements of phosphorus along a chronosequence of soils developed in an arid ecosys-

tem. The movement of phosphorus was compared with the movements and losses of other elements derived from parent material, and the relative contributions of biotic factors and geochemical factors in immobilizing phosphorus within the system were measured. Overall changes in forms and amounts of phosphorus were compared with other indicators of weathering and pedogenic development. In addition, the effects of the changing availability and chemical forms of phosphorus on phosphorus concentrations in plant species along the chronosequence were studied.

SOIL DEVELOPMENT IN AN ARID ECOSYSTEM

In the deserts of the Basin and Range Province of the southwestern United States, fault-bounded north–south–trending mountain ranges separate broad linear valleys. Individual alluvial fans and channels are clearly visible near the bases of the mountains. These fans coalesce downslope to form fairly uniform, shallow-sloped alluvial surfaces known as bajadas, or fan piedmonts (Thornbury 1969).

A generalized model of soil deposition and formation on piedmont slopes in an arid environment is shown in Fig. 1. During the late Pleistocene with a climate generally characterized by increased moisture (Gile 1966, Nettleton et al. 1975, Van Devender and Spaulding 1979, Wells 1979, 1983), sedimentation/erosion cycles deposited alluvium derived from mountain bedrock across a relatively broad piedmont surface. During subsequent periods of landscape stability, well-developed Aridisols formed with characteristic soil horizons (Ruhe 1975, Birkeland 1984). Red to reddish-brown horizons of silicate clay accumulation (argillic Bt horizons) formed by clay eluviation from surface horizons as well as by in situ weathering of parent material minerals (Gile and Grossman 1968, Nettleton

et al. 1975). The reddish color of these argillic horizons is due to the oxidized iron compounds that form from the weathering of mafic minerals. These oxyhydroxides initially precipitate as metastable, poorly crystalline particles known as ferrihydrite (Schwertmann and Fischer 1973). The crystallinity of these oxyhydroxides increases with increasing soil age (McFadden 1982). Calcium carbonate accumulates in the lower horizons of arid soils, forming petrocalcic or caliche (Bkm) horizons at extreme stages of development. Calcium (or $CaCO_3$) deposited at the soil surface from rainfall and eolian dust is also carried to lower soil horizons by percolating rainwater. Since calcium and bicarbonate ions move through the soil in dissolved form, these ions are transported further than clays and precipitate as calcium carbonate below the zone of clay deposition (Gile et al. 1981).

During the relatively dry and warm conditions of the Holocene (Irwin-Williams and Haynes 1970, Van Devender 1977), sedimentation/erosion cycles produced alluvium that buried older soils but that did not, on average, travel as far down the slope as Pleistocene material. Due to a relatively short interval for soil formation, argillic and calcic horizons are less well developed in Holocene deposits. As these soils formed under a regime of less available soil water than those developed during the Pleistocene, the formation of argillic horizons has been slower, and calcic horizons have formed closer to the soil surface (Nettleton et al. 1975, Marion et al. 1985). Progressively younger deposits show progressively weaker horizon development and less evidence of weathering of parent alluvial materials.

STUDY AREA

This study was conducted on the Jornada Experimental Ranch of New Mexico State University in the Jornada Del Muerto Basin, 40 km north-northeast of Las Cruces, New Mexico, an area near the northern limits of the Chihuahuan Desert. The Jornada Basin is located in the Mexican Highland section of the Basin and Range physiographic province. Geomorphic surfaces in this area were initially defined and studied by Ruhe (1967) and were later studied in detail as part of the Desert Soil–Geomorphology Project of the United States Soil Conservation Service (Gile et al. 1981).

The chronosequence of soils studied occurs on the piedmont slope of Mount Summerford in the Dona Ana Mountains, near the western boundary of the Jornada Basin. These mountains represent a fault block uplift within the Rio Grande rift of southern New Mexico (Seager et al. 1976). Extensive rhyolite lavas and tuffs have filled a subsided cauldron and are intruded by a series of monzonite porphyry and rhyolitic dikes. Mount Summerford is formed by a large monzonite mass and is essentially laccolithic in geometry. Soils on the piedmont slopes of this mountain show no signs of alluvial input from other sources. The permanent

transect of the Desert Long Term Ecological Research (LTER) is also situated along this slope. The climate is arid, with potential evapotranspiration exceeding 10 times the annual precipitation. Rainfall below 1500 m elevation averages 16–20 cm/yr, with more than half the precipitation occurring during July–September (Gile et al. 1981).

Several geomorphic surfaces of distinct age have been described along this slope and identified as a chronosequence of soils from a single parent material by Gile et al. (1981). The topographic position of this slope allows no other sources of alluvium except that derived from Mount Summerford.

The oldest soils along this transect form the Jornada II geomorphic surface. These soils are thought to be the product of several episodes of erosion and deposition over a period ranging from middle Wisconsinan to pre-Wisconsinan time (Table 1), and thus are thicker and more widespread than successive soil surfaces. Erosional surfaces in small drainageways alternate with broad areas of higher, uneroded soils. These soils show distinct horizons of clay and calcium carbonate accumulation characteristic of Pleistocene age soils.

Isaack's Ranch soils are presumed to have been deposited during one or more relatively dry periods near the end of the last glacial pluvial cycle, at the boundary of the late Wisconsinan–early Holocene. Soil stabilization and horizon formation may have occurred during a pluvial substage of this period. This geomorphic unit forms a discontinuous surface generally confined to individual fan drainageways that locally bury Jornada II soils. Horizons of clay and carbonate accumulation are not as well developed as in older Pleistocene soils but are better developed than in younger Holocene soils.

The youngest soils along this chronosequence form the Organ geomorphic complex. Although these soils cannot be placed into the specific subcategories of Gile et al. (1981), the soils were categorized as Organ I (early Holocene) and Organ II (late Holocene), on the basis of distinct Holocene age geomorphic surfaces that were visible along this sequence. Soil profiles on the youngest geomorphic surface, Organ II, contain high percentages of coarse gravel derived from the initial weathering of monzonite. These soils show little visible evidence of pedogenic alteration. Organ I soils show distinct but relatively weakly developed argillic and calcic horizons. Below a depth of ≈50 cm, argillic and calcic horizons of Pleistocene age soils can be found, demonstrating that this Organ I surface buries the Jornada II surface.

Plant communities also vary along this chronosequence transect, most probably due to past land-use history (Buffington and Herbel 1965, Stein and Ludwig 1979). Organ II soils and upper Organ I soils support mixed forb and grass communities, with a black grama association (primarily *Bouteloua eriopoda* Torr. and *Eragrostis curtipendicellata* Buckl.) in the upper pied-

TABLE 1. Characterization and estimated ages (yr BP) of soils from four geomorphic surfaces in the Jornada chronosequence.

Soil	Characterization	Estimated age (Gile et al. 1981)	^{14}C age, carbonate horizon (this study)
Late Organ (Organ II)	coarse-loamy, mixed thermic Ustollic Haplargids	1100–2200	3040 (60–80 cm)
Early Organ (Organ I)	coarse-loamy, mixed thermic Typic Haplargids	2200–7000	3800 (B2k horizon)
Isaack's Ranch	coarse-loamy, mixed thermic Typic Haplargids	8000–15 000	12 270 (B3k horizon)
Jornada II	fine-loamy, mixed thermic Typic Haplargids	25 000–75 000	25 660 (B4k horizon)

mont and a fluffgrass (*Tridens pulchellus* [H.B.K.] Hitchc.) association lower down the slope. Middle Organ I soils support a *Larrea tridentata* (DC.) Cov. shrub community with few forbs in intershrub spaces. Lower Organ I soils, Isaack's Ranch, and Jornada II soils represent a disturbed grassland community dominated by *Croton pottsii* (Klotzsch) Muell. Arg., *Aristida longiseta* Steud., and *Bouteloua* species.

METHODS

Field sampling and soil analyses

At least five soil pits were dug in each of the four geomorphic surfaces along the chronosequence. Several subjective criteria were used for the general placement of pits. Topographic highs were selected near the centers of the mapped geomorphic surfaces, thereby avoiding areas of drainage or erosion. Individual pits were placed approximately in the centers of these areas and at a distance of at least 10 m from any other pit in order to sample the mapped geomorphic surface adequately. If evidence of ancient arroyo systems or extensive erosion appeared in subsurface horizons of any pit, the pit was abandoned and a new area was chosen. Pits were dug to a minimum depth of 1 m or until a caliche horizon was encountered. Soil horizons were identified in each pit and their depths and thicknesses were measured (Lajtha 1986).

Soil samples were collected by genetic horizon in the Organ I, Isaack's Ranch, and Jornada II pits. Genetic horizons could not be identified in the Organ II soils, and thus samples were collected by depth interval. At least 1 kg of dry soil was collected from each horizon and was stored in a plastic bag. Several large blocks of unexposed rock material from Mount Summerford were obtained by breaking exposed boulders and removing material at least 5 cm inside the observable weathering rind.

Subsamples of unsieved soils from the lowest carbonate horizon of pits in each of the soil ages were taken for ^{14}C dating (Teledyne Isotopes Incorporated). All remaining soils were sieved to pass a 2-mm mesh screen. Particle size analyses were made using the hydrometer method, with a 2-h reading for clay content (Day 1965). Carbonate determinations were made by

weighing the water displaced by evolved CO_2 after soils were treated with 6 mol/L HCl (Horton and Newsom 1953). Organic carbon was determined by a modified Walkley-Black technique after acid pretreatment to remove carbonates (Allison 1960) by the Agronomy Analytical Laboratory of Cornell University.

For all other chemical analyses, rocks and soils were powdered in a Spex 8000 mixer-mill to pass a 150-μm mesh screen.

Total element analyses

Total element analyses were performed using a lithium borate fusion in purified graphite crucibles (Thompson and Walsh 1983). A flux mixture of 2:1 $Li_2B_4O_7 : LiBO_4$ was used, and the glass bead was dissolved in a 5% HNO_3 solution. Na and K in the solution were determined using a Perkin-Elmer 370 Atomic Absorption Spectrophotometer. Fe, Al, Ti, Ca, and Mg analyses were made on a Perkin-Elmer 6000 Inductively Coupled Plasma Emission Spectrometer (ICP) using Sc as an internal standard. Total P in the solution was determined using the molybdate-ascorbic acid procedure on a Technicon AutoAnalyzer II (Lennox 1979).

Phosphorus fractionation

Phosphorus fractionation was performed using a slight modification of the sequential extracting technique of Hedley et al. (1982). Although those authors used only ground soil, both ground and unground soil were used in this experiment to determine if mineral surfaces that are exposed upon grinding contribute phosphorus that would not ordinarily be available to the soil solution. Only inorganic fractions were measured, as the organic C content of the soils was extremely low. One gram of ground soil or 2 g of unground soil were extracted with 30 mL of each solution. All extractions were carried out in polyethylene centrifuge tubes that were shaken constantly for 16 h. Tubes were then centrifuged at 10 g for 8 min and the supernatant was decanted and saved.

The most biologically labile forms of inorganic P were extracted with Dowex 1-X8 anion exchange resin in the bicarbonate form enclosed in nylon mesh (Amer

TABLE 2. Soil particle size analyses. Organ II is the youngest soil; soil age increases in the indicated sequence. Data are means ± SE.

Soil	Soil horizon	% coarse	% of <2 mm fraction		
			Sand	Silt	Clay
Organ II	A	31.57	72.68 ± 0.78	18.54 ± 2.17	7.06 ± 0.34
	8–20 cm	33.12 ± 2.91	74.73 ± 1.71	16.72 ± 1.51	8.56 ± 0.36
	20–30 cm	28.74 ± 0.36	73.55 ± 1.27	17.96 ± 0.91	8.50 ± 0.53
	30–45 cm	32.97 ± 1.96	74.93 ± 0.68	16.66 ± 0.50	8.41 ± 0.32
	45–60 cm	38.76 ± 0.97	78.98 ± 2.16	13.90 ± 1.59	7.12 ± 0.81
	60– cm	37.41 ± 0.73	74.76 ± 3.18	15.52 ± 0.79	9.72 ± 2.47
Organ I	A	15.23 ± 2.34	79.80 ± 1.29	14.30 ± 1.31	5.89 ± 0.54
	B1t	5.19 ± 0.26	79.59 ± 0.29	11.72 ± 0.39	8.69 ± 0.17
	B2k	16.06 ± 1.54	73.00 ± 0.82	14.78 ± 0.62	12.22 ± 0.53
	B3k	15.79 ± 5.33	70.35 ± 4.37	14.20 ± 0.38	15.44 ± 4.30
	B4k	22.76	68.71	13.04	18.25
Isaack's Ranch	A	3.80 ± 0.20	76.59 ± 2.26	15.24 ± 2.05	8.23 ± 0.39
	B1t	9.50 ± 2.31	75.60 ± 0.62	10.74 ± 0.23	13.66 ± 0.55
	B2k	15.72 ± 1.59	71.57 ± 0.89	10.97 ± 0.87	17.46 ± 0.57
	B3k	14.27	72.69 ± 0.93	13.10 ± 1.34	14.21 ± 0.41
Jornada II	A	6.17 ± 1.24	80.30 ± 1.03	10.65 ± 1.01	9.05 ± 0.40
	B1t	6.78 ± 0.43	67.62 ± 0.45	13.98 ± 0.54	18.40 ± 0.50
	B2k	11.87 ± 1.96	62.80 ± 2.38	14.05 ± 0.63	23.15 ± 2.69
	B3k	17.11 ± 1.30	63.79 ± 1.79	10.63 ± 0.57	23.78 ± 1.29
	B4k	17.50 ± 2.12	64.80 ± 3.53	13.61 ± 1.28	21.59 ± 2.31

et al. 1955, Sibbesen 1978). P was later desorbed from the resin using 0.5 mol/L HCl. Labile P sorbed onto soil surfaces was then removed with 0.5 mol/L NaHCO₃ buffered to pH 8.5 (Olsen et al. 1954, Bowman and Cole 1978). This was followed by a 0.1 mol/L NaOH extraction to remove amorphous and some crystalline Fe and Al phosphates, as well as P strongly bound by chemisorption to Fe and Al compounds (Ryden et al. 1977, Williams et al. 1980). After the initial 16-h extraction, the solution was ultrasonified for 60 s with a small probe to extract P held on the internal surfaces of soil aggregates. This solution was then shaken for an additional 4 h. Relatively insoluble Ca-P minerals, including apatite, were extracted with 1 mol/ L HCl (Williams et al. 1971). Residual P was calculated as the difference between total P from fusion analyses and the sum of the extracted P fractions.

Results were expressed both as the absolute amount of P and as the percent of total P in the soil that was extracted in each step.

Organic and microbial phosphorus

The organic phosphorus content of eight soil samples from each of the four soil ages was measured using the dry-ashing technique of Saunders and Williams (1955). Soils were collected in July 1985 when relatively dry, and thus this measure of organic P represents the pool of P in relatively stable organic matter. Ignited and nonignited samples were extracted with 0.5 mol/L H₂SO₄ for both 2 and 24 h.

The more labile pool of microbial P was measured during the dry season and during several periods of the wet season at one site in Organ I soils during the sum-

mer and fall of 1985. A modification of the chloroform fumigation techniques of Brookes et al. (1982) and Hedley and Stewart (1982) was followed, in which 2 mL of CHCl₃ were added to 20 g of sieved, unground soil in large centrifuge bottles. Bottles were capped and allowed to incubate for 4 h, after which, caps were removed and the CHCl₃ was allowed to evaporate in a fume hood overnight. Control soils were treated in the same manner except for the addition of CHCl₃. Microbial biomass P was calculated as the difference in anion resin extractable P in fumigated vs. unfumigated soils. The fraction of biomass P made extractable by CHCl₃ (K_P) was taken to be 0.4, the mean value found in a variety of soils by both Brookes et al. (1982) and Hedley and Stewart (1982).

Plant phosphorus availability

Plant phosphorus availability along the chronosequence was estimated by measuring resin-available P (Binkley and Matson 1983) and by an in situ plant bioassay. Resin bags of a 50-cm² area contained 4 g of Dowex 1-X8 anion exchange resin (300–850 μm) in undyed stocking material. Resins were converted to the bicarbonate form using 0.5 mol/L NaHCO₃ prior to placement in the field. Five bags were buried just below the A horizon in each of nine locations on the LTER transect along this chronosequence. Bags were replaced every 10 wk for 18 mo. Bags were rinsed thoroughly in deionized water and spun dry for storage prior to analysis. The resin material was desorbed in 0.5 mol/L HCl and the solution was analyzed for PO₄ using standard autoanalysis procedures (Lennox 1979).

Two shrub species in the genus Gutierrezia, G. microcephala (DC.) Gray and G. sarothrae (Pursh) Britt

& Rusby, grow in small washes and alluvial channels on the bajada. Samples of green leaf tissue of both species were collected from several plants at ≈5-m intervals along the transect at the end of the growing season in early summer. Tissues were ground in a Wiley Mill, digested in a Technicon block digestor using a sulfuric acid–hydrogen peroxide flux (Lowther 1980), and analyzed for total nitrogen and phosphorus using standard methods (Technicon 1977). The N:P ratio of leaf tissue was used as an approximate index of the relative availabilities of the two elements in the soil.

Iron and aluminum oxyhydroxides

An oxalate extraction solution described by Mc-Keague and Day (1966; 0.2 mol/L ammonium oxalate buffered to pH 3 with 0.2 mol/L oxalic acid) was used to estimate the paracrystalline ferrihydrite content of soils (Fe_2O_3o, or simply Fe_o). The total secondary, or "free" iron and aluminum oxyhydroxide content of soils was estimated as dithionite-extractable Fe and Al (Fe_d and Al_d: Holmgren 1967). Magnetite was removed using a hand magnet prior to both extractions to avoid Fe dissolution from magnetite during the oxalate extraction (McFadden and Hendricks 1985). Fe and Al in both extracts were analyzed by ICP.

Statistical analyses

The GLM procedure of SAS (SAS 1982) was used to perform all analyses of variance on unbalanced data sets. When the GLM indicated statistical significance, Tukey's HSD studentized range test was used to separate differences among categories. When values from A and B1t horizons were combined in total element analyses to examine changes in the upper profile as a whole, pits that did not have both horizons analyzed were excluded to avoid a horizon bias in comparisons of soil age.

In order to include Organ II soil horizons, which were sampled by depth, with other soil ages in by-horizon GLM analyses, five soil horizon levels were defined: horizon 1 = all A horizons; horizon 2 = B1t horizons and the 8–30 cm Organ II horizons; horizon 3 = B2k horizons and the 30–60 cm Organ II horizons; horizon 4 = B3k horizons and the 60– cm Organ II horizons; and horizon 5 = B4k horizons.

RESULTS

Soil dating and soil physical properties

Radiocarbon ages of $CaCO_3$ in three of the four geomorphic surfaces were within the range of ages, although generally at the younger end, estimated by Gile et al. (1981) from pedogenic characteristics (Table 1). The ^{14}C date for Organ I soils, however, appeared to be unrealistically young. Soils in this landscape position showed evidence of slight erosion during both the Holocene and the Pleistocene, and thus the sampled carbonate horizon was significantly shallower than sampled carbonate horizons in the other three soils,
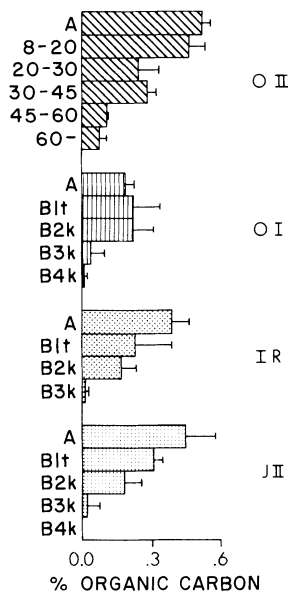

FIG. 2. Percent organic carbon ($\bar{X} \pm$ SE) in soil horizons from each of the four geomorphic surfaces. Each of the four large blocks of horizontal bars represents a soil geomorphic age, arranged from the youngest at the top to the oldest surface at the bottom of the chart. Within each block, individual bars represent analyses from soil horizons, extending from the surface A horizon to the lowest horizon sampled; horizons in Organ II are given as depths in centimetres. Note that the two lowest horizons in Organ I soils represent buried Pleistocene-age soils (cf. Fig. 1). O II = Organ II, O I = Organ I, IR = Isaack's Ranch, and J II = Jornada II.

and was partially coincident with the rooting zone of *Larrea* shrubs. Even slight contamination by modern $^{14}CO_2$ from root respiration could significantly affect measured ^{14}C ages in soil $CaCO_3$. In all soils, ^{14}C estimates from calcic horizons represent weighted average to young ages with respect to the age of initial soil deposition, as carbonate deposition proceeds continuously through soils over a relatively long period of time (Schlesinger 1985).

The gravel content of upper soil horizons decreased with increasing soil age, as well as increasing distance from the mountain pediment, from >30% in Organ II soils to <10% in the oldest Pleistocene soil (Table 2). Particle size distributions of the <2-mm soil fraction within the soil profile also varied along the chronosequence. All soils showed increasing clay accumulation with depth, with the most significant increase being between the A horizon and the next sampled horizon (the 8–30 cm zone in Organ II soils and the B1t horizon in older soils). The relative magnitude of this midprofile accumulation compared with surface horizons increased with increasing soil age, from just under 3% in the youngest soils to over 9% in the oldest soils.

Organic carbon content in surface soils did not vary consistently with soil age (Fig. 2). Surface horizon organic C content was highest in the youngest soils, but
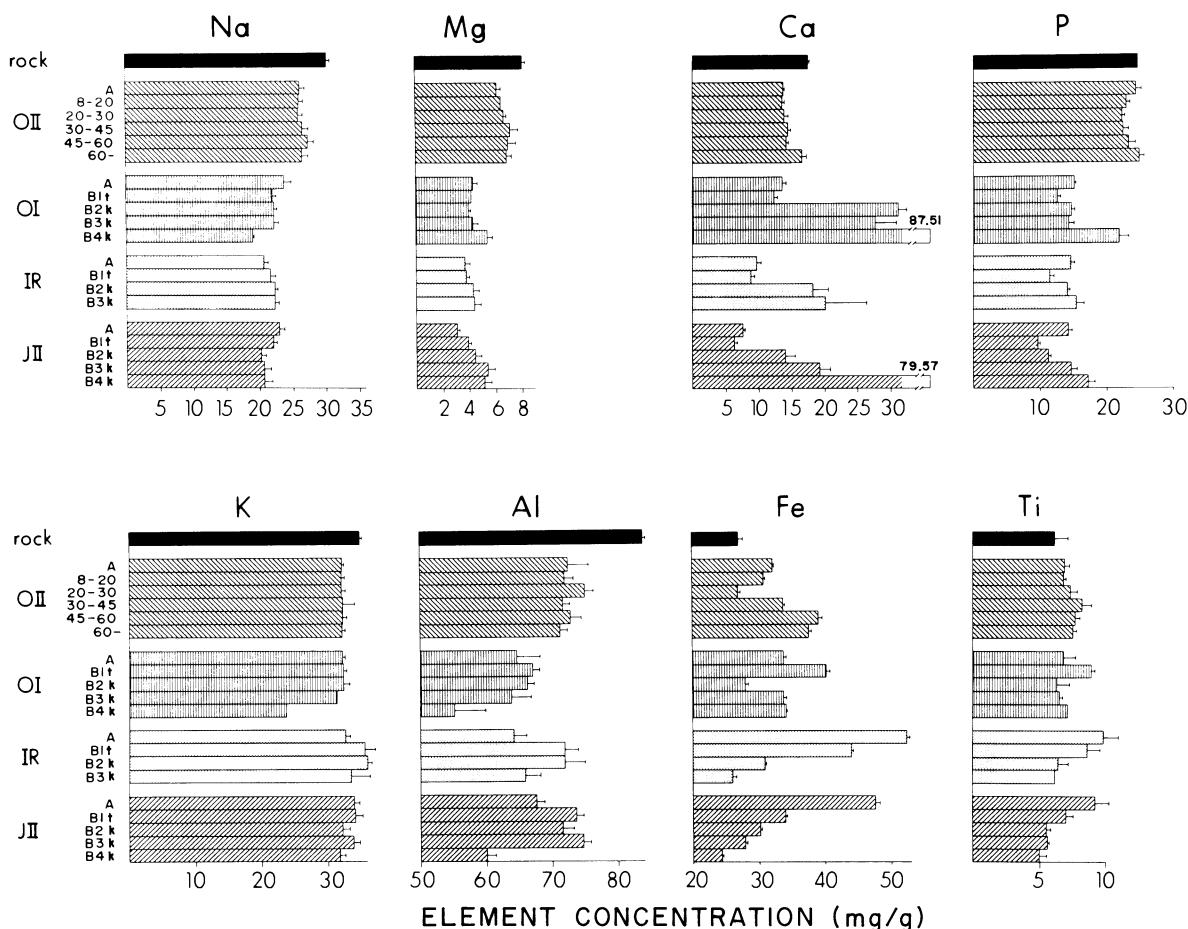
FIG. 3. Total element analyses of parent rock material (quartz monzonite) and soil horizons in each of the four geomorphic surfaces ($\bar{X} \pm$ SE). The top solid bars represent element analyses of monzonite from Mount Summerford. Abbreviations as in Fig. 2.

was lowest in the Organ I soils that are also of Holocene age. All values were quite low, with contents never exceeding 0.6% of the total soil mass.

Based on degree of clay translocation and depth to carbonate, soils were classified as suborders of Aridisols (Table 1).

Element profile data

Comparisons of surface horizons among soil ages show that concentrations of Na, Mg, and Ca decreased with soil age (Fig. 3). The concentration of K, however, remained relatively unchanged from the parent rock to the oldest Pleistocene soil. Ca clearly accumulated in lower horizons, mostly as precipitated $CaCO_3$ (Fig. 4). The movement and accumulation of Mg into lower horizons was not as pronounced as with Ca, suggesting that much of the Mg weathered from surface horizons was leached from the system. Na did not accumulate in lower horizons at all, and thus losses from surface horizons were translated into losses from the zone of biological activity in the ecosystem.

Concentrations of Al, Ti, and Fe showed different patterns of element redistribution within soil profiles and across soil ages. Although all soils showed lower Al concentrations than parent rock, there was no apparent decrease in concentration of Al in surface horizons with increasing soil age. Rather than accumulating in the lower horizons, Al showed a concentration increase in midprofile horizons even in the youngest soil. These increases were coincident with Bt horizons, or horizons of maximum clay accumulation.

Fe and Ti showed similar patterns of redistribution and accumulation that were different from patterns seen for the base cations and for Al. Surface horizons showed high concentrations in most soil ages, and these values tended to increase with increasing soil age. The surface accumulations of Fe can be mostly attributed to free magnetite, which was clearly visible in small arroyos or drainageways on the soil surface. The spatial heterogeneity of these channels and small fans on the bajada probably accounted for much of the variability in the Fe concentration data.

Concentrations of Fe and Ti in these soils were highly correlated ($r^2 = 0.67$). As magnetite usually contains a small percentage of Ti by mass, some of the Ti was directly linked with Fe. However, X-ray diffraction of magnetite collected from soil surfaces did not show the presence of Ti-Fe minerals such as ilmenite, and thus the similarities in Ti and Fe movements in the soil cannot be completely attributed to chemical linkage. Thin sections of rocks from Mount Summerford show the presence of sphene, a relatively heavy Ca-Ti silicate mineral. Dense, sphene-rich particles were probably transported in small alluvial channels in the same manner as magnetite-rich particles.

The loss and redistribution of P was similar to the pattern for Ca. Both showed midprofile decreases relative to surface horizons, and higher concentrations with depth. Below, phosphorus fractionation data are used to show that the Ca and P patterns are due to chemical links, such as P sorption onto $CaCO_3$ or the precipitation of secondary Ca-P minerals.

In summary, Ca, Mg, and P were the most easily lost elements from surface horizons (A and B1t horizons, or to a depth of 30 cm in Organ II soils), followed by Na, Al, and K. Fe showed an apparent net increase in concentration due to the magnetite accumulations in soils near the base of the bajada.

Phosphorus fractionation

Phosphorus fractions in ground and unground soils were very similar. HCl extracted a slightly larger percentage of total P in the ground soils, especially in the youngest soil horizons, probably due to the greater amount of primary apatite exposed upon grinding these soils. Similarly, the amount of P extracted by resins was significantly higher in ground than in unground soils. Statistical analyses were performed on data from ground soils to conform with other investigators using this fractionation technique (e.g., Tiessen et al. 1983, 1984). As results were similar when all soil horizons were combined or when only surface horizons were analyzed, only statistical analyses for surface horizons are presented.

There were no significant differences between the absolute amounts or the percent of total P extracted by resins across the chronosequence of soils (Table 3). In the ground soils, resins extracted 1–7% of the total P. Bicarbonate extracted less P than did resins, with values never exceeding 2% of total P. Labile P, the sum of resin- and bicarbonate-extractable P, never exceeded 8% of the total amount of P, and did not demonstrate a significant trend with soil age.

NaOH also extracted very little P, again with values never exceeding 1.2% of the total P in any of the soils. Neither the absolute amount nor the percent of total P extracted by NaOH demonstrated a significant trend with age. Although the highest absolute amount of NaOH-extractable P was in the Organ II soils, the highest percentages of total P were extracted in Jornada II
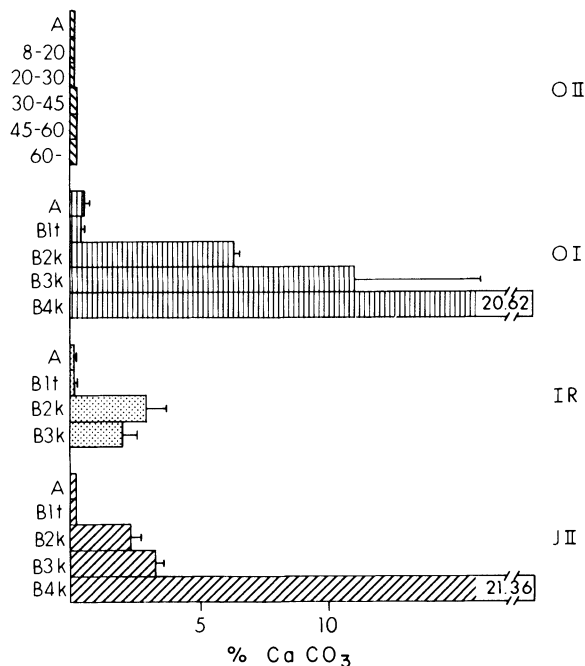

FIG. 4. Percent $CaCO_3$ ($\bar{X} \pm$ SE) in soil horizons from each of the four geomorphic surfaces. Abbreviations as in Fig. 2.

soils. The HCl extraction produced the largest P fraction in all soils, with most values exceeding 50% of total P. Both the absolute amount and the percent of total P extracted by HCl decreased significantly with each increase in soil age. Similarly, percent residual P increased significantly with soil age.

Surface horizons and the lowest calcic horizons showed the highest absolute amounts and percentages of labile forms of P (Table 4). The NaOH fraction decreased with increasing depth in all soils, with the strongly cemented calcic horizons having <0.2% of total P in this fraction. The maximum values for HCl-extractable P in each of the soil geomorphic ages occurred in the lowest calcic horizons, with the lowest values occurring in noncalcic, midprofile argillic horizons.

Soil organic and microbial phosphorus

Soil organic P content was below detection limits of the dry-ash technique for all soils along the chronosequence. Of the total P content of the soils, 60–90% was extracted in the 2-h acid extraction procedure. A high inorganic P extraction efficiency makes it difficult to measure low levels of organic P using this technique. Assuming an average soil organic C : organic P ratio of 120, the organic P content of surface Organ II soils, which had the highest organic C contents of all soils along the transect, would be 50 μg/g soil, or <5% of the total P content.

Microbial biomass P in these soils never exceeded 3% of the total P content, even in the middle of the

TABLE 3. Phosphorus fractionation data of combined surface horizons (A and B1t horizons, or to a depth of 30 cm). Data are means ± SE. Values within columns with different superscript letters have significantly different means at $P < .05$ (Tukey's HSD following ANOVA).

| | Extractant* | | | | |
	Resin	HCO₃	NaOH	HCl	Residual
	P in fraction (µg/g soil extracted)				
Organ II	24.62 ± 1.74	4.92 ± 0.88	12.89ᴬ ± 2.06	863.18ᴬ ± 28.10	274.39ᴮ ± 21.30
Organ I	26.55 ± 8.58	3.85 ± 0.78	4.91ᴮ ± 0.56	487.20ᴮ ± 21.52	184.69ᴬ ± 12.44
Isaack's Ranch	24.74 ± 6.25	4.18 ± 1.02	6.79ᴬᴮ ± 1.33	386.73ᴮᶜ ± 19.28	222.85ᴬᴮ ± 23.95
Jornada II	29.72 ± 8.91	4.59 ± 1.29	7.30ᴬᴮ ± 1.61	336.03ᶜ ± 44.59	237.53ᴬᴮ ± 11.22
Soil age $P =$	NS	NS	.0117	.0001	.0378
	Percent of total P				
Organ II	2.08 ± 0.12	0.41 ± 0.06	1.08 ± 0.15	73.23ᴬ ± 1.61	23.20ᴬ ± 1.52
Organ I	3.61 ± 1.07	0.54 ± 0.10	0.69 ± 0.07	68.96ᴬᴮ ± 1.99	26.20ᴬᴮ ± 1.79
Isaack's Ranch	3.80 ± 0.98	0.62 ± 0.12	1.01 ± 0.15	60.44ᴮᶜ ± 2.88	34.13ᴮᶜ ± 2.70
Jornada II	4.41 ± 1.06	0.68 ± 0.15	1.12 ± 0.17	53.66ᶜ ± 2.65	40.13ᶜ ± 3.81
Soil age $P =$	NS	NS	NS	.0001	.0011

  * Extraction sequence is described in Methods: Phosphorus Fractionation.

wet season (Table 5). Microbial P contents in wet soils after individual storm events were not significantly different from dry season values. Only after several rainfall events, when the soil had been wet for over a week, did microbial biomass P increase significantly. It was only during such periods that P held by microbes exceeded resin-extractable P.

Plant nutrient availability indices

The percent N, percent P, and the N:P ratio of *Gutierrezia* leaves showed no consistent trend with soil age or distance along the transect (Fig. 5). There was no significant difference in nutrient content between the two species across the sites.

An analysis of the accumulation of PO₄ in buried resin bags showed that values for individual 10-wk collections formed two groups, corresponding to the wet season (September–January) and the dry season (February–August). PO₄ accumulation during the wet season was highest in two sites in Organ II soils, but did not show a consistent trend with soil age and was not correlated with total P. With the exception of the two extreme sites where PO₄-P averaged 500 $\mu g \cdot bag^{-1} \cdot collection^{-1}$ during the wet season, all other

TABLE 4. Phosphorus fractionation data by horizon, all soil ages combined. Data are means ± SE. Analyses and presentation as in Table 3.

| | Extractant† | | | | |
Horizon*	Resin	HCO₃	NaOH	HCl	Residual
	Percent of total P				
1	4.65ᴬ ± 0.58	0.78ᴬ ± 0.06	1.25ᴬ ± 0.10	63.89ᴬᴮ ± 1.56	29.43ᴮ ± 1.23
2	2.62ᴮ ± 0.45	0.36ᴮ ± 0.02	0.83ᴮ ± 0.07	62.53ᴬᴮ ± 3.03	33.66ᴬᴮ ± 2.88
3	2.79ᴬᴮ ± 0.28	0.33ᴮ ± 0.02	0.45ᶜ ± 0.05	58.72ᴬ ± 2.69	37.71ᴬ ± 2.69
4	2.39ᴮ ± 0.46	0.39ᴮ ± 0.02	0.33ᶜᴰ ± 0.06	66.61ᴮᶜ ± 2.06	30.28ᴮ ± 2.03
5	4.04ᴬᴮ ± 0.54	0.90ᴬ ± 0.18	0.19ᴰ ± 0.07	73.22ᶜ ± 1.66	21.66ᶜ ± 1.71
Horizon $P =$	.0037	.0001	.0001	.0001	.0001
Soil age × horizon $P =$	NS	.0001	.0301	.0279	.0115
	P in fraction (µg/g soil extracted)				
1	38.39ᴬ ± 3.41	6.70ᴮ ± 0.42	11.43ᴬ ± 1.37	580.08ᴮ ± 55.17	260.40ᴬ ± 18.52
2	18.91ᴮ ± 3.05	2.70ᶜ ± 0.31	6.69ᴮ ± 1.30	489.99ᶜ ± 65.90	233.97ᴬ ± 18.73
3	20.73ᴮ ± 2.57	2.34ᶜ ± 0.12	3.46ᶜ ± 0.63	449.81ᶜ ± 60.08	266.11ᴬ ± 12.64
4	19.86ᴮ ± 3.39	3.29ᶜ ± 0.28	3.04ᶜ ± 0.80	569.62ᴮ ± 61.88	247.53ᴬ ± 12.82
5	39.24ᴬ ± 6.76	8.16ᴬ ± 1.38	2.03ᶜ ± 0.85	708.58ᴬ ± 51.58	207.56ᴬ ± 16.48
Horizon $P =$	.0001	.0001	.0001	.0001	.0309
Soil age × horizon $P =$	NS	.0001	NS	.0001	NS

  * New soil horizon levels defined so as to include the Organ II horizons, which were sampled by depth: 1 = all A horizons; 2 = B1t and the 8–30 cm Organ II horizons; 3 = B2k and the 30–60 cm Organ II horizons; 4 = B3k and the 60− cm Organ II horizons; 5 = B4k horizons.
  † Extraction sequence is described in Methods: Phosphorus Fractionation.

TABLE 5. Microbial biomass P estimates, calculated as the percent of total P in the soil and relative to resin-extractable P. Data are means ± SE.

	Microbial biomass P (μg/g soil)	% of total P	Microbial P ÷ resin-extractable P
Dry season			
Mean, July 1985			
A horizon	5.34 ± 1.40	0.71 ± 0.19	0.41 ± 0.11
Small storms			
6 August 1985			
A horizon	2.71 ± 1.89	0.36 ± 0.25	0.27 ± 0.16
4 September 1985			
A horizon	4.15 ± 0.34	0.54 ± 0.21	0.40 ± 0.16
Bt horizon	3.92 ± 0.52	0.52 ± 0.07	0.67 ± 0.11
Wet season			
20 September 1985			
A horzion	20.12 ± 4.24	2.68 ± 0.57	1.64 ± 0.30
Bt horizon	3.68 ± 0.80	0.49 ± 0.11	0.61 ± 0.14

sites averaged 90 μg·bag^{-1}·collection^{-1}. There were no significant differences between sites during the dry periods of the year when all ion accumulation values were very low.

Iron and aluminum oxyhydroxides

Concentrations of oxalate-extractable iron (Fe$_o$) and dithionite-extractable iron (Fe$_d$) and aluminum (Al$_d$) all increased with increasing soil age along this chronosequence (Table 6). Values from B4k horizons, Pleistocene caliche layers, were all very low and were excluded from this analysis to prevent a strong horizon bias in comparisons across soil ages.

Dithionite-extractable iron tended to be more highly correlated with specific phosphorus fractions than was oxalate-extractable iron. Fe$_d$ was significantly negatively correlated with the percent of total P in the HCl fraction ($P < .0001$, $r^2 = 0.63$) and was positively correlated with the percent in the residual P fraction ($P < .0001$, $r^2 = 0.62$). The correlation with HCl-extractable P was lower ($P < .0001$, $r^2 = 0.04$), and the correlation with residual P disappeared when absolute amounts of P were used in the regression. Fe$_d$ was weakly negatively correlated with both absolute amounts and the percent of total P in the bicarbonate fraction, as well as with absolute amounts of resin-extractable P ($P < .0006$, .04, .33, and $r^2 = 0.22, 0.08,$ 0.15, respectively). The only significant correlation between Fe$_o$ and any P fraction was a weak positive relationship between Fe$_o$ and the percent of total P extracted by resins ($P < .02$, $r^2 = 0.11$).

DISCUSSION

Total chemical analysis coupled with the mass balance approach is perhaps the most accurate way of determining the amount of chemical weathering and ion movement that has taken place within an ecosystem (McFadden 1982, Schimel et al. 1985). In this chronosequence of soils, however, as in many sequences formed on alluvial piedmont surfaces, the mass balance approach could not be used due to erosional losses of some soils. The relatively thin Pleistocene Bt horizon underlying the Holocene soils of Organ I age compared with the thickness of the same Bt horizon in Jornada II soils is strong evidence of the erosional removal of soils from upper slope positions in sparsely vegetated arid systems. Without knowing the absolute depths of soil horizons prior to erosion, it is not possible to convert chemical concentration data to total profile contents and thus calculate absolute losses and gains of elements from the system.

The loss of elements from rocks or soil profiles by weathering affects the calculation of the relative percentages of elements in the remaining material. Similarly, the input of a constituent into a soil horizon, such as illuvial CaCO$_3$, will appear to dilute the concentrations of elements in that horizon. A common way to estimate absolute weathering losses and to avoid these apparent concentration changes is to divide the concentration of elements in weathered material by the concentration of an index element whose content can be assumed not to change. Authors have used both Al, which is relatively insoluble in the normal soil pH range of 4–9 (Birkeland 1984), and Ti, which is insoluble above pH 4.5 and which has been shown to be quite immobile in calcareous soils (Bachman and Machette 1977). Although this ratio technique has been shown to be accurate in measuring chemical weathering losses from rocks, in arid soils Al is redistributed within the soil profile (Fig. 3), and Ti moves within the soil as a metal particulate. Thus in this study, analyses are given in mass percentages, and only relative increases and decreases in concentrations can be calculated.

Many factors affect the weathering and subsequent leaching of ions from an ecosystem. Parent material
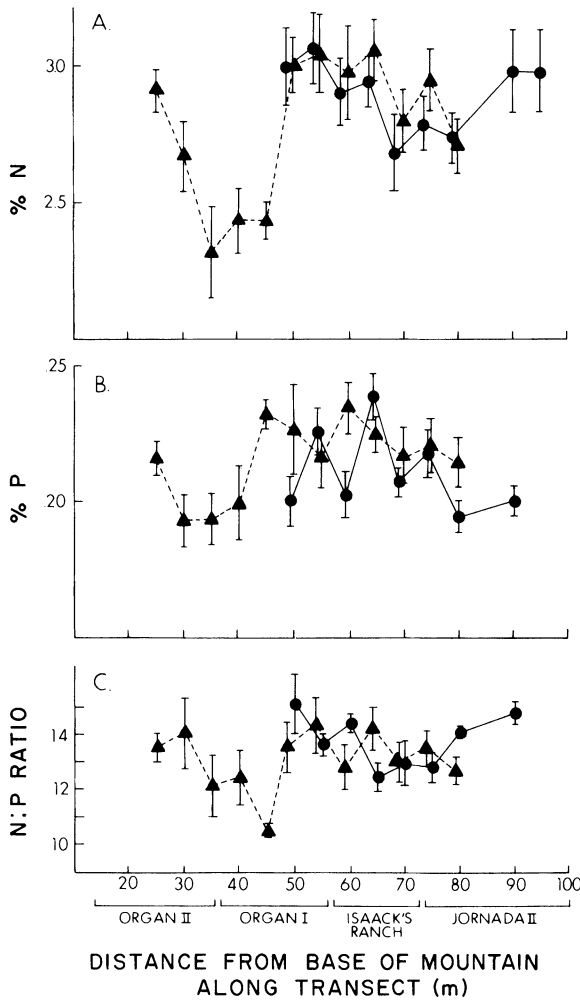
FIG. 5. (A) %N, (B) %P, and (C) N:P ratio ($\bar{X} \pm$ SE) in leaves of *Gutierrezia sarothrae* (●) and *G. microcephala* (▲) along the Mount Summerford transect.

composition is of primary importance, as minerals vary significantly in their resistance to weathering. Similarly, ion retention and leaching losses are controlled by the formation of secondary clays and oxides that persist in soils. The relative stability of Al and Si is certainly partially due to the precipitation of resistant aluminosilicate minerals; Fe and Al also form stable secondary hydrous oxides. Base cation losses from an ecosystem are also dependent on secondary clays that form in soils. Miller and Drever (1977) found that ferromagnesian minerals were readily weathered from andesitic rock, but retention by secondary clays made Mg the least mobile of the elements in the watershed.

Vegetation can also affect ion retention within soils (Reynolds and Johnson 1972, Vitousek and Reiners 1975). Smyth (1913) attributed the relatively low concentrations of K in riverflow to plant uptake and retention. Barshad (1964) suggested that plant uptake could seasonally control the cation content and pH of soils, and thus cause different clays to form at different times in the year.

Two different techniques are used to calculate relative weathering losses of elements from both rocks and whole ecosystems (Table 7). The first technique, the one used in this study, is to locate a chronosequence of soils or a weathering sequence of saprolite and measure the elemental content of soils relative to the parent material. The second technique is to measure element concentrations in rivers that drain closed watersheds where bedrock composition is known.

The soil chronosequence approach has the disadvantage that intact weathering sequences are hard to identify, and thus somewhat unorthodox methods are often used to rank soils according to age. The watershed approach has the disadvantage that river water chemistry can vary significantly over different seasons, in part due to biotic uptake and release of nutrients (Cleaves et al. 1970, Reynolds and Johnson 1972). In addition, it is often not possible to identify all source rocks in an ecosystem that contribute to weathering losses in stream water. Sedimentary rocks and evaporites in the ecosystem will also affect the apparent resistance of ions to weathering loss.

Despite these inherent problems, and the variations induced by differences in parent material, climate, and vegetation, ion mobility sequences found in different ecosystems by different methods tend to agree fairly closely (Table 7). Ca and Na are generally the most easily lost elements along with Mg, while K tends to be the least easily leached of the base cations. Although P is rarely measured in these sequences, it appears to be less easily removed than base cations but is more readily leached than Al, Ti, or Si.

In this study, the relative ion loss sequence from monzonite in an arid system was Ca = Mg = P > Na > Al > K > Fe, based on removals from surface horizons (Fig. 5). This loss sequence does not, however, take into account whether ions weathered from surface horizons accumulate in lower horizons, move down the landscape, or are lost from the system through leaching. Mg and P accumulate at depth relative to concentrations in surface horizons, whereas Na and K do not. Na might thus be lost from the ecosystem as a whole more readily than P and Mg, which in turn might be more readily lost than K, Fe, and Al. It is difficult to precisely place Ca into this sequence, as the input of Ca into the system from dustfall and precipitation is quite large in arid ecosystems that have sparsely vegetated, dry soils, especially in the proximity of uplifted limestone mountains. Gile et al. (1981) calculated the average rate of $CaCO_3$ added from current atmospheric sources as $\approx 2 \text{ g} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$, and stated that atmospheric additions rather than weathering releases of Ca are the main source of $CaCO_3$ in caliche horizons.

Similarly, the incorporation of externally derived eolian dust could be a significant input of new clay material into these soil profiles (Gile 1975, McFadden

TABLE 6. Analysis of variance and Tukey's HSD analysis of extractable iron and aluminum oxyhydroxides by soil age, all horizons except Pleistocene B4k horizons included. Data are means ± SE. Values within each column with different letters have significantly different means at $P < .05$.

Soil	Fe_o (mg/g)	Fe_d (mg/g)	Al_d (mg/g)
Organ II	5.82[A] ± 0.59	23.50[AB] ± 0.62	2.91[AB] ± 0.12
Organ I	6.22[AB] ± 0.90	22.42[A] ± 0.73	2.72[A] ± 0.09
Isaack's Ranch	7.51[AB] ± 1.45	28.20[B] ± 1.72	3.39[B] ± 0.28
Jornada II	9.51[B] ± 0.88	35.61[C] ± 1.59	4.04[C] ± 0.15
Soil age P	.0166	.0001	.0001

1982). A large input of externally derived clay could significantly affect the interpretation of the chemical weathering sequence in this study. For instance, it is possible that some of the observed K^+ stability over the chronosequence is due to inputs to the older soils of illite or muscovite, both rich in K^+. Attempts to approximate prehistoric rates of eolian input in arid regions based on present rates have been largely unsuccessful (Gile et al. 1981), as it is highly unlikely that rates of input under past climates can be estimated from rates under present climatic conditions (McFadden 1982). The amount of input will certainly be dependent on landscape position and the composition of surrounding parent material sources. For surfaces that are topographic highs, such as the piedmont slope of this study, the rate of deflation weathering might be expected to exceed the rate of dust input, but it is generally difficult to distinguish areas that are net sinks for dust from areas that are net sources. If most local source material is compositionally similar to the orig-

inal parent material of the soil, then the main effect of dust influx would be to lessen the observed degree of chemical weathering. However, the potential for significant amounts of eolian clay influx is certainly an inherent error in measurements of chemical changes with soil weathering in arid regions.

In the weathering sequence calculated in this study, P is lost from the system as readily as the most easily leachable cations. This result is not in accord with data of Goldich (1938) or Hendricks and Whittig (1968), or the fact that of all major nutrients essential to plant growth, phosphorus is generally very tightly conserved in forest ecosystems (Wood et al. 1984). It is possible that the relative degree of plant cover, and thus the potential for biotic conservation, plays a major role in the difference between this arid ecosystem and more humid systems. However, it is also possible that in a high pH soil, where the activities of Fe and Al are greatly reduced, soil P fixation is also greatly reduced.

The apparent correlations between Ca and P distri-

TABLE 7. Ion weathering loss sequences based on soil chronosequences and on streamwater chemistry.

Stability sequence (easily weathered → resistant)	Parent material	Reference
Soil sequences		
Na > Ca > K > Al > Ti > Si > Fe > Mg	andesite, Absaroka Mts., Wyoming (clay data)	Miller and Drever 1977
K > Na > Al > Ti > Ca > Si > Fe > Mg	andesite, Absaroka Mts., Wyoming (bulk soils)	Miller and Drever 1977
Mg > Ca > K > Na = P > Si > Ti > Fe > Al > Mn	hypersthene andesite, Southern Cascades, California	Hendricks and Whittig 1968
Ca > Mg > Na > K > P > Si > Mn > Ti > Al > Fe	olivine andesite, Southern Cascades, California	Hendricks and Whittig 1968
Na > Ca > Mg > K > P > Si > Al	Morton gneiss	Goldich 1938
Ca > Na > Mg > Si > P > Al > K	amphibolite	Goldich 1938
Ca > Mg > K > Na > Si > Al > Fe	Medford diabase	Goldich 1938
Ca = Mg = P > Na > Al > K > Fe	quartz monzonite, New Mexico (surface horizon loss)	this study
Rivers and streams		
Ca > Na > Mg > K > Si > Fe > Al	igneous rocks, worldwide	Polynov 1937
Mg > Ca > Na > K > Si > Fe = Al	Littleton schist, Oliverian granite, Black Mt. granite in New Hampshire and Vermont	Anderson and Hawks 1958
Ca ≥ Na > Mg > Si ≥ K > Fe ≥ Al	granite rocks (general), Sierra Nevada	Feth et al. 1964
Ca > Mg > Na > Si = K > Fe > Al	quartz monzonite, Sierra Nevada	Feth et al. 1964
Na > Ca > Mg > K > Si > Fe > Al	granodiorite, Sierra Nevada	Feth et al. 1964
Ca > Na > Mg > K > Si > Fe = Al	igneous and sedimentary rocks, worldwide	Smyth 1913
Ca > Na ≥ Mg > K > Al = Si	Littleton formation, Hubbard Brook, New Hampshire	Likens et al. 1977
Ca > Mg > Na > K > Si > Fe	granitic rocks, worldwide	Holland 1978

bution patterns within soil profiles were confirmed by fractionation data, which showed that >50% of the total P in most soils was Ca-bound P. Although the chemical transformations of P in this arid system did not completely agree with the Walker and Syers (1976) model, many of the predicted trends were found. Total P decreased fairly rapidly over the chronosequence. Although >50% of the total P in most soils was Ca-bound P, this fraction decreased with increasing soil age as in their model, presumably due to the weathering of primary apatite P. However, the increase in the Ca-P fraction in lower calcic horizons suggests a secondary precipitation of Ca-P minerals or strong sorption reactions of P with precipitated $CaCO_3$. Total P increased in these calcic horizons relative to midprofile horizons, also suggesting that pedogenic carbonates have a strong geochemical role in the retention of P within the soil. In contrast to the Walker and Syers (1976) model, however, Fe- and Al-bound P were not significant fractions even in the oldest Pleistocene soils, and there were no correlations between extractable Al and Fe oxides and either total soil P or any extractable phosphorus fraction.

These results are in accord with those of Tiessen et al. (1984) who analyzed phosphorus fractions in 168 United States Department of Agriculture benchmark soils across eight soil orders representing a weathering sequence. In their study, 21% of the total P in highly weathered Ultisols was in the Fe- and Al-bound fraction, with an average of 5% of total P in the Ca-P form. Mollisols, at the other end of their weathering sequence, had only 6% of total P in the Fe- and Al-bound form, while 27% was in the Ca-bound form. The Aridisols of this study showed a higher percent of total P in the Ca form, which could be due to either a low weathering intensity in arid systems or the fixation of P by pedogenic carbonates. Similarly, Roberts et al. (1985) demonstrated that as pH increased across several climo-toposequences in Canada, the relative proportion of Ca-bound P increased and the proportion of Fe- and Al-bound P decreased. These authors attributed both the change in pH and in P fractions to changes in weathering intensity.

In a regression analysis examining soil characters and P fractions, Tiessen et al. (1984) found that the percent of HCl-extractable P was highly correlated to $CaCO_3$ content. In A-horizon soils, $CaCO_3$ content was the major negative regression variable for labile inorganic P. These results are consistent with the generalization that $CaCO_3$ stabilizes P in calcareous soils, and that the presence of $CaCO_3$ in surface horizons reduces labile, or plant-available P.

The total P content of soils in this study was not related to organic carbon content, as had been suggested by Walker and Adams (1958) and Walker and Syers (1976). Although organic carbon content was highest in the youngest soils of Organ II age that also

had the highest total P content, Organ I soils, also of Holocene age, had relatively high levels of P and the lowest organic carbon content. It appears more likely that both slope position and vegetation type control the carbon content of soils along this transect. The low organic C content of Organ I soils could certainly be related to erosion of soils in this landscape position, as discussed earlier. In addition, middle Organ I soils support an evergreen *Larrea* shrub community with only sparse forb cover in intershrub spaces. It is also possible that the low organic carbon content of these soils is due to lower organic matter input from the *Larrea* community compared with the mixed forb and grass communities of soils both higher and lower on the slope transect.

Similarly, there was little evidence for the stabilization of P in these soils by soil organic matter. Decomposition of fallen leaf material is fairly rapid in this arid ecosystem (Whitford et al. 1981), and P retranslocation by the dominant plant species is quite high, yielding litter with a relatively low P content (Lajtha 1987). It is not surprising that organic P could not be measured in these soils that had an organic C content of <0.6%. It is similarly unlikely that the biotic uptake of P by plants is a significant stabilizer of P in this ecosystem. Assuming annual plant uptake equal to annual litterfall plus root turnover and a lower rooting zone of 50 cm, the ≈30 kg/ha of P of plant uptake (calculated from a litterfall value of 15 $kg\cdot ha^{-1}\cdot yr^{-1}$ [W. G. Whitford, *personal communication*] and an equal input from root turnover [P. J. Fonteyn, *personal communication*] is a small percentage of the 5×10^3 kg/ha of total P found within the rooting zone in even the oldest soils along this chronosequence.

During most of the year when soils are dry, microbial P is a very small pool. However, during the autumn rain season, which is also the season of the greatest litterfall (Burk and Dick-Peddie 1973), P held by microbes exceeded extractable P, suggesting that microbes might compete effectively with plants for labile P. Although microbial immobilization of P might play an important role in the biotic cycling of P within the system, it does not appear to be a significant overall pool for P in these soils, as microbial biomass P never exceeded 3% of the total P content. These results are in sharp contrast with those from highly organic soils. In peat soils of the southeastern coastal plain, Walbridge (1986) found that microbial P accounted for 36–55% of total soil P. Chapin et al. (1978) demonstrated that cycling of P in Alaskan tundra was largely dependent on microbial population dynamics, with labile P being released only during episodic population crashes.

Although the total P content of these soils decreased with increasing soil age, neither the total P content nor the N:P ratio of *Gutierrezia* shrubs changed across the transect. Similarly P availability measured by field-placed resin bags did not appear to be related to the

total P content of the soils, just as the resin or resin + HCO$_3$ percentages of total P in the soils did not vary with soil age in the P fractionation experiments.

Conclusions

In a chronosequence of soils developed from quartz monzonite alluvium in southwestern New Mexico, changes in forms and amounts of phosphorus were found to vary predictably over time. Total P in the soil profile decreased with increasing soil age, and was removed from surface horizons as readily as the most easily leachable base cations. As predicted by the Walker and Syers (1976) model, Ca-bound forms of P decreased with increasing soil age. However, throughout the chronosequence Ca-bound P remained the single largest fraction of total P and was greatest in the most strongly calcic horizons. In contrast, Fe- and Al-bound P did not increase over time, but remained as a very small percent of the total P in all soils. Similarly, soil organic P never represented a significant pool of P, and labile forms of P represented only a small proportion of the total P in these soils.

Organic carbon accumulation and forms and amounts of P in the soil appeared to be relatively unrelated. Soil organic carbon was more related to vegetation type and landscape position than to P content. Similarly, nutrient availability was not well correlated with soil age or total amounts of P, and P concentrations in shrubs did not reflect the changing forms or amounts of P.

There seemed to be little evidence for biological conservation of P within this ecosystem. Although microbial biomass P may have an important role in biotic P availability, both total soil organic P and microbial P represented a very small pool of the total P.

The biogeochemical cycle of P in these soils is quite different from the cycle in more mesic, forested ecosystems. In Spodosols of the Hubbard Brook Experimental Forest, Wood et al. (1984) demonstrated that upper soil horizons represented a zone of biological control over the movement and loss of P from the ecosystem. Lower horizons, with high concentrations of free iron and aluminum, represented a zone of strong geochemical fixation that effectively controlled the loss of P to stream-water leaching. While pedogenic CaCO$_3$ appears to be the main geochemical factor retaining P within the soil profile in Aridisols, P was not as tightly conserved as in more mesic, acidic forested ecosystems.

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