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September 1988 Vol. 146, No. 3 Printed in U.S.A.

# FACTORS AFFECTING PHOSPHATE SORPTION AND PHOSPHATE RETENTION IN A DESERT ECOSYSTEM

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In a study of soils from a chronosequence in southern New Mexico, where CaCO3 accumulation is primarily derived from aeolian input, P adsorption was greatest in the most highly calcic horizons and least in horizons of clay and oxyhydroxide accumulation. Similarly, adsorption capacity was most highly correlated with CaCO<sub>3</sub> content. Iron and Al oxyhydroxide contents increased with increasing soil age, and absolute levels were as high as in calcareous soils developed in more humid conditions. Calcium carbonate appears to be the primary geochemical agent capable of the fixation and retention of P within the soil profile in this ecosystem.

Sorption and desorption reactions between phosphate and soils have long been studied by soil scientists, but have only recently been examined by ecosystem ecologists to explain phosphorus movement and phosphorus retention within ecosystems. In both temperate and tropical forest ecosystems, phosphate is very tightly conserved within soil compartments (Laverdiere 1982; Wood et al. 1984), and loss of phosphorus in stream water is generally very low (Goldich 1938; Hendricks and Whittig 1968; Wood et al. 1984).

Phosphorus is geochemically fixed in soils through interactions with calcium-, aluminum-, and iron-phosphate minerals (Lindsay and Moreno 1960; Marion and Babcock 1977). Iron and Al sesquioxides can cause high levels of P fixation in highly weathered or acidic soils. In Spodosols of the Hubbard Brook Experimental Forest, Wood et al. (1984) demonstrated that phosphorus adsorption capacities were highly correlated with concentrations of HCl-extractable Fe and Al. Richardson (1985) demonstrated that P

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Received for publication 20 March 1987; revised 19 Aug. 1987.

sorption and retention capacity were best predicted by concentrations of amorphous Al in many wetland ecosystems.

Adsorption of P onto CaCO<sub>3</sub> and the coprecipitation of Ca-P minerals occur in both alkaline aquatic and terrestrial systems (Cole and Olsen 1959; Holford and Mattingly 1975a; Avnimelech 1983). Similarly, Tiessen et al. (1984) and Lajtha and Schlesinger (1988) suggest that Ca-bound forms of P constitute the dominant pool of mineral soil P in arid and semiarid soils of the southwestern United States. However, several P adsorption studies in calcareous soils derived from limestone have found stronger relationships between P adsorption capacity and hydrous oxides of Fe and Al than with CaCO3 content (Holford and Mattingly 1975b; Ryan et al. 1985). Perhaps part of this discrepancy may be explained by differences between calcareous soils derived from limestone parent materials and arid soils in which the presence of high levels of CaCO3 is due to pedogenic accumulations of aeolian-derived salts. Arid-land soils are relatively less weathered and thus pedogenically younger than soils developed in more humid climates, and thus one might expect lower accumulations of oxidized Fe and Al compounds (Olsen and Watanabe 1957). In addition, the nature and form of Fe and Al oxyhydroxides could be qualitatively different in arid soils and soils of humid regions. Initially weathered Fe oxyhydroxides occur as paracrystalline, highsurface-area particles known as ferrihydrite (Schwertmann and Fischer 1973). Over time, ferrihydrite recrystallizes to more stable and more highly crystalline forms, such as goethite and hematite. The timing of these transformations depends, however, on ambient climatic conditions.4 These different crystalline forms of oxidized Fe and Al could vary in their ability to fix soil P (Ryan et al. 1985).

The purpose of this study was to identify the primary geochemical agent capable of retaining

<sup>4</sup> L. D. McFadden, 1982, The impacts of temporal and spatial climatic changes on alluvial soils' genesis in southern California, Diss., Univ. of Arizona, Tucson, Arizona.

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P within an arid ecosystem in southern New Mexico. To accomplish this objective, the amounts and relative proportions of paracrystalline and total secondary Fe and Al oxyhydroxides were measured along a chronosequence of soils derived from quartz monzonite, and the relative importances of these oxyhydroxides and pedogenic CaCO<sub>3</sub> in P adsorption and P accumulation within the soil profile were assessed.

#### **METHODS**

# Study site

Soils for this study were collected along a piecimont slope of Mt. Summerford in the Jorel Muerto Basin, 40 km NNE of Las Cruces, New Mexico, an area near the northern limits of the Chihuahuan Desert. The permanent transects of the Desert Long Term Ecological Research site (LTER) of New Mexico State University are also situated along this bajada. Several geomorphic surfaces of distinct ages have been identified along this slope (Table 1: Fig. 1; Gile et al. 1981) and form a four-stage soil chronosequence. The youngest soils are of Holocene age and form the Organ geomorphic complex. Organ II soils show little visible evidence of pedogenic alteration, high percentages of coarse gravel, and relatively high levels of organic matter. Organ I soils show distinct but relatively weakly developed horizons and contain less organic matter in upper horizons, possibly due to the erosional nature of soils in this landscape position. The oldest soils along this slope form the Jornada II geomorphic surface. These soils show distinct horizons of clay accumulation (argillic, or Bt horizons) overlying zones of CaCO<sub>3</sub> accumulation (caliche, or Bk horizons), characteristic of Pleistocene-age soils. Isaack's Ranch soils are presumed to have been

deposited near the end of the last glacial pluvial cycle and form a discontinuous surface that locally buries Jornada II soils. Horizons of clay and carbonate accumulation are not as well developed in these soils as in older Pleistocene soils, but are better developed than in Holocene soils.

## Field sampling and soil analysis

Five soil pits were dug in each of the four geomorphic surfaces along the chronosequence to a minimum depth of 1 m or until a caliche horizon was encountered. Soil samples were collected by genetic horizon in the Organ I, Isaack's Ranch, and Jornada II pits, and by depth interval in Organ II soils. All soils were sieved to pass a 2-mm-mesh screen, to screen out the relatively large chunks of unweathered parent rock material that are found in these soils. Carbonate determinations were made by weighing the water displaced by evolved CO2 after soils were treated with 6 M HCl (Horton and Newsom 1953). The percentage of 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. Bicarbonateextractable P was determined according to methods of Olsen et al. (1960). Total soil P analyses were performed using a lithium borate fusion in graphite crucibles (Thompson and Walsh 1983), followed by colorimetric determination using an automated molybdate-ascorbic acid procedure on a Technicon AutoAnalyzer (Lennox 1979).

#### Extractable Fe and Al

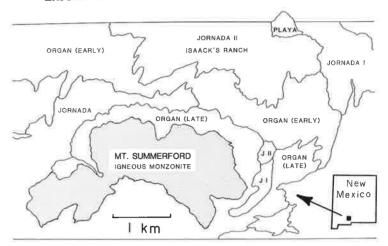
Soils were powdered in a Spex 8000 mixermill to pass a 100-mesh screen prior to Fe and Al extraction. An oxalate extraction solution

TABLE 1
Soil chemical properties (means with one standard deviation in parentheses), to a depth of 30 cm, and estimated ages for four geomorphic surfaces in the Jornada chronosequence

Soil	Estimated age, yr BP <sup>a</sup>	Organic carbon, %	Bicarbonate-extractable P, µg/g
Late Organ	1100-2200	0.41 (.07)	10.5 (4.3)
(Organ II)			
Early Organ	2200-7000	0.21 (.08)	7.0 (2.6)
(Organ I)			
Isaack's Ranch	8000-15 000	0.31 (.11)	8.1 (3.1)
Jornada II	25 000-75 000	0.33 (.12)	6.8 (2.2)

<sup>&</sup>lt;sup>a</sup> Gile et al. (1981).

FIG. 1. Soil geomorphic surfaces along the piedmont of Mt. Summerford in southern New Mexico. JII = Jornada II; JI = Jornada I; Jornada = undifferentiated Jornada deposition. Isaack's Ranch surface forms a discontinuous surface that locally buries the Jornada II surface and thus is not mapped separately.



described by McKeague and Day (1966; 0.2 M ammonium oxalate buffered to pH 3 with 0.2 M oxalic acid) was used to estimate the paracrystalline ferrihydrite content of soils (Fe<sub>0</sub>). The total secondary, or total "free," Fe and Al content of soils was estimated as dithionite-extractable Fe and Al (Fe<sub>d</sub> and Al<sub>d</sub>; 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 on a Perkin-Elmer 6000 inductively coupled plasma emission spectrometer (ICP). The ratio of Feo to Fed was calculated as an index of the degree of crystallinity of secondary oxyhydroxides.

# Phosphorus adsorption capacity

Phosphate solutions, ranging in concentration from 0 to 30 µg P/ml as KH<sub>2</sub>PO<sub>4</sub> in 0.02 M CaCl<sub>2</sub>, were added to 3 g of sieved, unground soil in 50-ml polypropylene centrifuge tubes with 1 drop of chloroform to give a soil:solution ratio of 1:10. Soil solutions were shaken for 96 h at 27°C and centrifuged at 5000 rpm for 10 min; P in the supernatant was determined using the molybdate-ascorbic acid procedure on a Technicon AutoAnalyzer (Lennox 1979). The adsorption capacity of soils  $(X_m)$  for each solution concentration (m) was calculated as the difference between the initial and the equilibrium solution P content and expressed as  $\mu g P/g$ soil. The phosphorus adsorption index  $(PAI_m)$ of Bache and Williams (1971) was calculated as  $X_m/\log(C_m)$ , where  $C_m$  = equilibrium solution P concentration in  $\mu g/L$  at an initial solution con-

centration of m. This index has been found to be highly correlated with the sorption maximum determined from Langmuir isotherm calculations (Bache and Williams 1971; C. J. Richardson unpublished data), with the advantage of needing fewer P solution points per soil to calculate the index. In addition, there are no inherent assumptions that the energy of adsorption does not vary with the surface coverage as in the Langmuir equation, an assumption that has been often questioned in empirical studies (Gunary 1970). As Bache and Williams (1971) also demonstrated a high correlation between absolute sorption capacity  $(X_m)$  at high initial solution additions (thus making it possible to ignore E, the initial amount of sorbed P in the soil) and the Langmuir adsorption maximum,  $X_{10}$ and  $X_{30}$  were similarly used as relative sorption indexes.

### Statistical analyses

As the number of soils within each soil age category was unequal, the GLM procedure of SAS (SAS Institute 1982) was used in lieu of the ANOVA procedure to analyze profile accumulation data. When the GLM procedure indicated statistical significance, Tukey's HSD range test was used to separate differences among geomorphic surfaces. The GLM procedure was used to perform all regressions with adsorption data.

#### RESULTS

The percentage of CaCO<sub>3</sub> was very low and did not vary with depth in the youngest Holocene soil (Table 2). In the three older soils,

Extractable Fe and Al oxyhydroxides and % CaCO $_3$  in soil horizons from soils of the four geomorphic units $^\circ$ TABLE 2

(1.08) 25.14 (0.98) 2.83 (0.13) 0.25 (0.03) 0.17 (0.03) 1.1 (0.44) 23.13 (1.58) 2.80 (0.28) 0.19 (0.01) 0.20 (0.02) 1.1 (0.77) 23.09 (1.01) 3.07 (0.34) 0.31 (0.09) 0.20 (0.02) 1.1 (0.07) 25.08 (3.81) 3.55 (0.73) 0.20 (0.01) 0.35 (0.08) 1.1 (1.00) 21.36 (1.05) 2.49 (0.11) 0.26 (0.04) 0.25 (0.02) 1.1 (1.00) 23.50 <b>AB</b> (0.62) 2.91 <b>AB</b> (0.12) 0.25 (0.04) 0.25 (0.02) 1.1 (0.59) 23.50 <b>AB</b> (0.62) 2.91 <b>AB</b> (0.12) 0.25 (0.03) 0.46 (0.05) 0.2 (0.19) 0.1 (0.22) 2.47 (0.25) 2.47 (0.06) 0.22 (0.08) 0.46 (0.05) 0.2 (0.09) 2.5.45 (1.75) 2.58 (0.03) 0.22 (0.03) 0.45 (0.05) 0.0 (0.24) 2.5.45 (1.75) 2.58 (0.03) 0.22 (0.03) 0.49 (0.01) 0.2 (0.24) 0.2 (0.25) 0.28 (0.04) 0.25 (0.08) 0.1 (0.24) 2.5.40 (1.76) 2.94 (0.05) 0.21 (0.07) 0.18 (0.11) 0.1 (0.24) 2.5.40 (1.76) 2.94 (0.05) 0.31 (0.07) 0.18 (0.11) 0.1 (0.24) 2.5.40 (1.76) 2.94 (0.05) 0.31 (0.07) 0.18 (0.11) 0.1 (0.24) 2.5.40 (1.76) 2.94 (0.05) 0.31 (0.07) 0.18 (0.11) 0.1 (0.24) 2.5.40 (1.76) 2.94 (0.05) 0.31 (0.07) 0.18 (0.11) 0.1 (0.24) 2.5.40 (1.76) 2.94 (0.05) 0.31 (0.07) 0.18 (0.11) 0.1 (1.78) 3.61 (0.07) 2.94 (0.05) 0.31 (0.07) 0.25 (0.03) 0.2 (0.24) 0.13 (0.24) 0.13 (0.07) 0.23 (0.01) 0.1 (1.78) 39.61 (0.51) 4.56 (0.28) 0.25 (0.03) 3.26 (0.25) 0.23 (0.03) 0.2 (0.25) 0.23 (0.01) 0.2 (0.21) 0.20 (0.21) 0.20 (0.21) 0.20 (0.21) 0.20 (0.21) 0.20 (0.21) 0.20 (0.21) 0.20 (0.25) 0.23 (0.02) 0.20 (0.25) 0.23 (0.03) 0.2 (0.25) 0.23 (0.03) 0.2 (0.25) 0.23 (0.03) 0.2 (0.25) 0.23 (0.03) 0.2 (0.25) 0.23 (0.03) 0.2 (0.25) 0.23 (0.03) 0.2 (0.25) 0.23 (0.03) 0.2 (0.25) 0.23 (0.03) 0.2 (0.25) 0.23 (0.03) 0.2 (0.25) 0.23 (0.03) 0.2 (0.25) 0.23 (0.03) 0.2 (0.25) 0.23 (0.03) 0.2 (0.25) 0.23 (0.03) 0.2 (0.25) 0.23 (0.03) 0.2 (0.25) 0.23 (0.03) 0.2 (0.25) 0.23 (0.03) 0.2 (0.25) 0.23 (0.03) 0.2 (0.25) 0.23 (0.03) 0.2 (0.25) 0.23 (0.03) 0.2 (0.25) 0.23 (0.25) 0		Horizon	Fe., m	mg/g	Fe <sub>a</sub> , m	mg/g	Ald, 12	g/gu	Fe	Fe,:Fe	CaCO <sub>3</sub> , %	3, %	Total F	Total P, mg/g
8–20 cm         4.33         (0.44)         23.13         (1.58)         2.80         (0.28)         0.19         (0.01)         0.20         (0.02)         1.145           20–30         6.95         (1.77)         23.09         (1.01)         3.07         (0.34)         0.20         (0.02)         1.107           30–45         5.04         (0.30)         24.84         (1.87)         3.25         (0.22)         0.20         (0.01)         0.25         (0.08)         1.107           45–60         7.14         (3.30)         24.84         (1.87)         3.25         (0.22)         0.20         (0.01)         0.25         (0.08)         1.107           60–100         5.58         (0.59)         23.50AB         (0.62)         2.91AB         (0.11)         0.26         (0.02)         1.157         1.171         (2.21)         2.49         (0.11)         0.26         (0.02)         1.157         1.171         1.151         2.94         (0.22)         0.02         (0.02)         1.157         1.151         2.94         (0.23)         0.25         (0.02)         1.157         0.25         (0.02)         1.159         0.25         0.020         0.020         0.020         0.020         0.	Organ II	A	6.25	(1.08)	25.14	(0.98)	2.83	(0.13)	0.25	(0.03)	0.17	(0.03)	1.225	(0.038)
20-30 6.95 (1.77) 23.09 (1.01) 3.07 (0.34) 0.31 (0.09) 0.20 (0.02) 1.107 45-60 7.14 (3.30) 23.08 (3.81) 3.55 (0.73) 0.20 (0.01) 0.25 (0.03) 1.119 0.20 (0.01) 0.25 (0.03) 1.119 0.20 (0.01) 0.25 (0.02) 1.107 0.20 (0.01) 0.25 (0.02) 1.236 (0.02) 1.236 (0.02) 1.236 (0.02) 1.236 (0.03) 1.236 (0.		8-20 cm	4.33	(0.44)	23.13	(1.58)	2.80	(0.28)	0.19	(0.01)	0.20	(0.03)	1.145	(0.023)
30-45   5.04   (0.37)   25.08   (3.81)   3.55   (0.73)   0.20   (0.01)   0.35   (0.08)   1.119   (0.110)   0.25   (0.08)   1.157   (0.110)   0.25   (0.02)   1.256   (0.02)		20-30	6.95	(1.77)	23.09	(1.01)	3.07	(0.34)	0.31	(0.03)	0.20	(0.05)	1.107	(0.022)
Mean   5.83   1.35   1.45   1.87   1.87   1.81   1.82   1.028   0.11   0.26   0.04   0.25   0.03   1.157     Mean   5.83   1.00   2.1.86   1.05   2.49   0.11   0.26   0.04   0.25   0.02   1.236     Mean   5.83   1.00   2.1.36   1.05   2.91   2.91   0.11   0.26   0.04   0.25   0.02   1.236     B		30-45	5.04	(0.97)	25.08	(3.81)	3.55	(0.73)	0.20	(0.01)	0.35	(0.08)	1.119	(0.034)
Mean   5.82A   (0.69)   21.36   (1.05)   2.49   (0.11)   0.26   (0.04)   0.25   (0.02)   1.236   (0.04)   (0.25)   (0.02)   (0.		45–60	7.14	(3.30)	24.84	(1.87)	3.12	(0.22)	0.28	(0.11)	0.25	(0.03)	1.157	(0.045)
Mean         5.82A         (0.59)         23.50AB         (0.62)         2.91AB         (0.12)         0.25         (0.02)           B1t         6.39         (2.21)         24.71         (1.15)         2.93         (0.23)         0.43         (0.13)         0.62         (0.19)         0.752           B2k         4.68         (0.70)         21.01         (0.25)         24.77         (0.06)         0.22         (0.03)         64.2         (0.21)         0.752           B3k         4.68         (0.70)         21.01         (0.25)         2.47         (0.06)         0.22         (0.03)         64.2         (0.21)         0.703           B3k         4.88         (0.70)         21.01         (0.25)         2.47         (0.06)         0.22         (0.05)         11.08         (0.21)         0.703           B3k         4.88         (0.75)         22.42A         (0.73)         2.72A         (0.92)         0.28         (0.05)         11.08         (5.81)         0.709           B1t         10.88         (3.26)         32.47         (0.36)         2.89         (0.31)         0.01         0.01         0.04         0.73         0.786         0.786         0.786 <td< td=""><td></td><td>60 - 100</td><td>5.53</td><td>(1.00)</td><td>21.36</td><td>(1.05)</td><td>2.49</td><td>(0.11)</td><td>0.26</td><td>(0.04)</td><td>0.25</td><td>(0.03)</td><td>1.236</td><td>(0.031)</td></td<>		60 - 100	5.53	(1.00)	21.36	(1.05)	2.49	(0.11)	0.26	(0.04)	0.25	(0.03)	1.236	(0.031)
A         8.98         (2.41)         21.71         (2.21)         2.94         (0.23)         0.43         (0.13)         0.62         (0.19)         0.752           B1t         6.39         (2.22)         24.71         (1.15)         2.93         (0.02)         0.25         (0.03)         0.46         (0.05)         0.621         0.651         0.631           B2k         4.68         (0.70)         21.01         (0.25)         2.47         (0.06)         0.22         (0.03)         6.42         (0.15)         0.631           B3k         4.88         (0.75)         22.85         (1.75)         2.58         (0.16)         0.22         (0.05)         11.08         (5.81)         0.799           Mean         4.87         (0.68)         2.72A         (0.05)         0.27         (0.05)         11.08         (5.81)         0.799           B1t         10.88         (3.26)         2.54         (0.73)         2.72A         (0.69)         0.21         (0.01)         0.72         (0.77)         0.74         0.77           B2k         4.37         (0.49)         0.31         (0.01)         0.25         (0.04)         0.25         (0.04)         0.74         0.74		Mean	5.82A	(0.59)	23.50AB	(0.62)	2.91AB	(0.12)	0.25	(0.02)		Ì		(=)
B1t   6.39   (2.22)   24.71   (1.15)   2.93   (0.02)   0.25   (0.08)   0.46   (0.05)   0.631   0.632   0.632   0.635	Organ I	Ą	8.98	(2.41)	21.71	(2.21)	2.94	(0.23)	0.43	(0.13)	0.62	(0.19)	0.752	(0.010)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		B1t	6.39	(2.22)	24.71	(1.15)	2.93	(0.02)	0.25	(0.08)	0.46	(0.02)	0.631	(0.018)
B3k         4.88         (0.75)         22.85         (1.75)         2.58         (0.16)         0.22         (0.05)         11.08         (5.81)         0.709           mch         A         4.88         (0.75)         22.42A         (0.73)         2.72A         (0.92)         0.28         (1.08)         (5.81)         0.706           mch         A         4.87         (0.60)         25.74         (0.36)         2.89         (0.31)         0.10         (0.02)         0.16         (0.08)         0.726           B1t         10.88         (3.26)         32.67         (3.47)         4.30         (0.49)         0.31         (0.07)         0.18         (0.11)         0.770           B2k         4.33         (0.24)         25.40         (1.76)         2.94         (0.05)         0.17         (0.01)         3.01         (0.74)         0.770           B3k         7.79         (1.39)         24.90         (4.31)         2.55         (0.32)         0.31         (0.01)         3.01         (0.74)         0.74         0.771         0.771           Mean         7.51AB         (1.45)         28.20B         (1.72)         3.38B         (0.24)         0.23         (0.01)<		B2k	4.68	(0.70)	21.01	(0.25)	2.47	(90.0)	0.22	(0.03)	6.42	(0.21)	0.732	(0.019)
Mean         6.22AB         (0.98)         22.42A         (0.73)         2.72A         (0.92)         0.28         (0.04)           anch         A         4.87         (0.60)         25.74         (0.36)         2.89         (0.31)         0.10         (0.02)         0.16         (0.08)         0.726           B1t         10.88         (3.26)         32.67         (3.47)         4.30         (0.49)         0.31         (0.07)         0.18         (0.11)         0.572           B2k         4.33         (0.24)         25.40         (1.76)         2.94         (0.05)         0.17         (0.01)         3.01         (0.74)         0.700           B3k         7.79         (1.39)         24.90         (4.31)         2.55         (0.32)         0.31         (0.01)         2.05         0.771           Mean         7.51AB         (1.45)         28.20B         (1.72)         3.39B         (0.28)         0.25         (0.03)         0.71         0.71           B1t         12.01         (1.78)         39.61         (0.51)         4.56         (0.18)         0.23         (0.04)         0.23         (0.03)         0.478           B2k         8.20         (0.71) </td <td></td> <td>B3k</td> <td>4.88</td> <td>(0.75)</td> <td>22.85</td> <td>(1.75)</td> <td>2.58</td> <td>(0.16)</td> <td>0.22</td> <td>(0.02)</td> <td>11.08</td> <td>(5.81)</td> <td>0.709</td> <td>(0.033)</td>		B3k	4.88	(0.75)	22.85	(1.75)	2.58	(0.16)	0.22	(0.02)	11.08	(5.81)	0.709	(0.033)
anch A         4.87         (0.60)         25.74         (0.36)         2.89         (0.31)         0.10         (0.02)         0.16         (0.08)         0.726           B1t         10.88         (3.26)         32.67         (3.47)         4.30         (0.49)         0.31         (0.07)         0.18         (0.11)         0.572           B2k         4.33         (0.24)         25.40         (1.76)         2.94         (0.05)         0.17         (0.01)         3.01         (0.74)         0.572           B3k         7.79         (1.39)         24.90         (4.31)         2.55         (0.32)         0.31         (0.01)         2.05         (0.56)         0.771           Mean         7.51AB         (1.45)         28.20B         (1.72)         3.39B         (0.28)         0.25         (0.03)         0.771         0.771         0.771         0.771         4.56         (0.18)         0.25         (0.03)         0.771         0.771         0.789         0.23         (0.04)         0.23         (0.071)         0.771         3.38         0.36         0.049         0.23         0.071         0.771         0.78         0.78         0.729         0.78         0.78         0.78		Mean	6.22AB	(0.98)	22.42A	(0.73)	2.72A	(0.92)	0.28	(0.04)			2	ì
B1t         10.88         (3.26)         32.67         (3.47)         4.30         (0.49)         0.31         (0.07)         0.18         (0.11)         0.572           B2k         4.33         (0.24)         25.40         (1.76)         2.94         (0.05)         0.17         (0.01)         3.01         (0.74)         0.700           B3k         7.79         (1.39)         24.90         (4.31)         2.55         (0.32)         0.31         (0.01)         2.05         (0.74)         0.700           Mean         7.51AB         (1.45)         28.20B         (1.72)         3.39B         (0.28)         0.25         (0.03)         2.05         0.771           A         10.57         (2.65)         27.85         (1.86)         3.68         (0.14)         0.37         (0.07)         0.23         (0.01)         0.771           B1t         12.01         (1.78)         39.61         (0.51)         4.56         (0.18)         0.30         (0.04)         0.23         (0.03)         0.478         (0.88)           B2k         8.20         (0.71)         40.00         (2.71)         3.87         (0.36)         0.22         (0.03)         2.35         (0.34)         0	Isaack's Ranch	A	4.87	(09.0)	25.74	(0.36)	2.89	(0.31)	0.10	(0.05)	0.16	(0.08)	0.726	(0.026)
B2k         4.33         (0.24)         25.40         (1.76)         2.94         (0.05)         0.17         (0.01)         3.01         (0.74)         0.700           B3k         7.79         (1.39)         24.90         (4.31)         2.55         (0.32)         0.31         (0.01)         2.05         (0.56)         0.771           Mean         7.51AB         (1.45)         28.20B         (1.72)         3.39B         (0.28)         0.25         (0.03)         2.05         0.771           A         10.57         (2.65)         27.85         (1.86)         3.68         (0.14)         0.37         (0.07)         0.23         (0.01)         0.711           B1t         12.01         (1.78)         39.61         (0.51)         4.56         (0.18)         0.30         (0.04)         0.23         (0.03)         0.478         (           B2k         8.20         (0.71)         40.00         (2.71)         3.87         (0.36)         0.21         (0.02)         2.35         (0.34)         0.562         (           B3k         6.95         (0.82)         32.91         (3.38)         3.99         (0.34)         0.22         (0.03)         2.36         (0.25)		B1t	10.88	(3.26)	32.67	(3.47)	4.30	(0.49)	0.31	(0.07)	0.18	(0.11)	0.572	(0.030)
B3k         7.79         (1.39)         24.90         (4.31)         2.55         (0.32)         0.31         (0.01)         2.05         (0.56)         0.771           Mean         7.51AB         (1.45)         28.20B         (1.72)         3.39B         (0.28)         0.25         (0.03)         2.05         (0.71)           A         10.57         (2.65)         27.85         (1.86)         3.68         (0.14)         0.37         (0.07)         0.23         (0.01)         0.711           B1t         12.01         (1.78)         39.61         (0.51)         4.56         (0.18)         0.30         (0.04)         0.23         (0.03)         0.478         (           B2k         8.20         (0.71)         40.00         (2.71)         3.87         (0.36)         0.21         (0.02)         2.35         (0.34)         0.562         (           B3k         6.95         (0.82)         32.91         (3.38)         3.99         (0.34)         0.22         (0.03)         3.26         (0.25)         0.729         (           B4k         6.41         (2.53)         14.35         (1.38)         1.49         (0.13)         0.44         (0.15)         0.27		B2k	4.33	(0.24)	25.40	(1.76)	2.94	(0.05)	0.17	(0.01)	3.01	(0.74)	0.700	(0.013)
Mean         7.51AB         (1.45)         28.20B         (1.72)         3.39B         (0.28)         0.25         (0.03)           A         10.57         (2.65)         27.85         (1.86)         3.68         (0.14)         0.37         (0.07)         0.23         (0.01)         0.711           B1t         12.01         (1.78)         39.61         (0.51)         4.56         (0.18)         0.30         (0.04)         0.23         (0.03)         0.478         (           B2k         8.20         (0.71)         40.00         (2.71)         3.87         (0.36)         0.21         (0.02)         2.35         (0.34)         0.562         (           B3k         6.95         (0.82)         32.91         (3.34)         0.22         (0.03)         3.26         (0.25)         0.729         (           B4k         6.41         (2.53)         14.35         (1.38)         1.49         (0.13)         0.44         (0.15)         21.36         (3.21)         0.862         (           Mean         9.51B         (0.88)         35.61C         (1.59)         4.04C         (0.15)         0.27         (0.02)         21.36         (3.21)         0.862         (     <		B3k	7.79	(1.39)	24.90	(4.31)	2.55	(0.32)	0.31	(0.01)	2.05	(0.56)	0.771	(0.053)
A         10.57         (2.65)         27.85         (1.86)         3.68         (0.14)         0.37         (0.07)         0.23         (0.01)         0.711           B1t         12.01         (1.78)         39.61         (0.51)         4.56         (0.18)         0.30         (0.04)         0.23         (0.03)         0.478           B2k         8.20         (0.71)         40.00         (2.71)         3.87         (0.36)         0.21         (0.02)         2.35         (0.34)         0.562           B3k         6.95         (0.82)         32.91         (3.38)         3.99         (0.34)         0.22         (0.03)         3.26         (0.25)         0.729           B4k         6.41         (2.53)         14.35         (1.38)         1.49         (0.13)         0.44         (0.15)         21.36         (3.21)         0.862           Mean         9.51B         (0.88)         35.61C         (1.59)         4.04C         (0.15)         0.27         (0.02)         21.36         (3.21)         0.862           p         0.02         0.0001         0.0001         0.0001         0.0001         0.0001         0.0001         0.0002         0.0001         0.018)		Mean	7.51AB	(1.45)	28.20B	(1.72)	3.39B	(0.28)	0.25	(0.03)				
12.01 (1.78) 39.61 (0.51) 4.56 (0.18) 0.30 (0.04) 0.23 (0.03) 0.478 8.20 (0.71) 40.00 (2.71) 3.87 (0.36) 0.21 (0.02) 2.35 (0.34) 0.562 6.95 (0.82) 32.91 (3.38) 3.99 (0.34) 0.22 (0.03) 3.26 (0.25) 0.729 6.41 (2.53) 14.35 (1.38) 1.49 (0.13) 0.44 (0.15) 21.36 (3.21) 0.862 9.51B (0.88) 35.61C (1.59) 4.04C (0.15) 0.27 (0.02) NS	Jornada II	A	10.57	(2.65)	27.85	(1.86)	3.68	(0.14)	0.37	(0.07)	0.23	(0.01)	0 711	(0.095)
8.20 (0.71) 40.00 (2.71) 3.87 (0.36) 0.21 (0.02) 2.35 (0.34) 0.562 (6.95 (0.82) 32.91 (3.88) 3.99 (0.34) 0.22 (0.03) 3.26 (0.25) 0.729 (6.41 (2.53) 14.35 (1.38) 1.49 (0.13) 0.44 (0.15) 21.36 (3.21) 0.862 (9.51B (0.88) 35.61C (1.59) 4.04C (0.15) 0.27 (0.02) NS		B1t	12.01	(1.78)	39.61	(0.51)	4.56	(0.18)	0.30	(0.04)	0.23	(0.03)	0.478	(0.011)
6.95 (0.82) 32.91 (3.38) 3.99 (0.34) 0.22 (0.03) 3.26 (0.25) 0.729 (6.41 (2.53) 14.35 (1.38) 1.49 (0.13) 0.44 (0.15) 21.36 (3.21) 0.862 (9.51B (0.88) 35.61C (1.59) 4.04C (0.15) 0.27 (0.02) NS		B2k	8.20	(0.71)	40.00	(2.71)	3.87	(0.36)	0.21	(0.03)	2.35	(0.34)	0.562	(0.017)
6.41 (2.53) 14.35 (1.38) 1.49 (0.13) 0.44 (0.15) 21.36 (3.21) 0.862 (9.51B (0.88) 35.61C (1.59) 4.04C (0.15) 0.27 (0.02) 0.0001 0.0001 NS		B3k	6.95	(0.82)	32.91	(3.38)	3.99	(0.34)	0.22	(0.03)	3.26	(0.25)	0.729	(0.039)
9.51B (0.88) 35.61C (1.59) 4.04C (0.15) 0.27 (0.02) 0.02 0.0001 0.0001 NS		B4k	6.41	(2.53)	14.35	(1.38)	1.49	(0.13)	0.44	(0.15)	21.36	(3.21)	0.862	(0.048)
0.0001 0.0001 NS		Mean	9.51B	(0.88)	35.61C	(1.59)	4.04C	(0.15)	0.27	(0.05)				Ē
10000		d	0.02		0.0001		0.0001		SN					

<sup>o</sup> Different letters within columns of oxyhydroxide data denote significantly different means by Tukey's HSD at alpha = 0.05; p values under each column are from analysis of variance comparisons of means of geomorphic units excluding B4k horizons. Values are means of n=5 (SE).

however, the percentage of  $CaCO_3$  increased with depth up to a maximum of >20% in the Pleistocene caliche (B4k) horizon. Organic C was very low in all soils, never exceeding 0.5% in surface horizons (Table 1). Bicarbonate-extractable P ranged from 10.5  $\mu$ g/g in the youngest soils to a mean of 7.3  $\mu$ g/g for the three older soils.

Concentrations of oxalate-extractable iron (Fe<sub>o</sub>) and dithionite-extractable iron (Fe<sub>d</sub>) and aluminum (Ald) increased with increasing soil age along the chronosequence (Table 2). This was true both when individual horizons and profile means were compared. Values for free Fe and Al from caliche horizons were very low, presumably due to precipitation at high pH levels near the surfaces of these horizons, and were excluded from this analysis to prevent a strong horizon bias in comparisons across soil ages. The Fe<sub>o</sub>:Fe<sub>d</sub> ratio did not show a clear pattern with soil age and varied around a mean value of 0.27. In the three soils with well-defined argillic (Bt) horizons, concentrations of Fe<sub>o</sub>, Fe<sub>d</sub>, and Ald all showed midprofile maximum values, with this pattern becoming more pronounced with

increasing soil age. Concentrations in Organ II profiles did not show such a clear redistribution pattern. Concentrations of Fe<sub>d</sub> and Fe<sub>o</sub> were significantly correlated in all soils (p < 0.0001, r = 0.53). Fe<sub>d</sub> and Al<sub>d</sub> were even more highly correlated (p < 0.0001, r = 0.88).

Concentrations of total P in surface soils decreased significantly with soil age (Table 2). In the three older soils there was a midprofile decrease in total P relative to surface horizons, followed by an increase in concentration with increasing depth. There were no significant correlations between total P accumulation and Fe $_{\rm o}$ , Fe $_{\rm d}$ , or Al $_{\rm d}$ , either alone or in multiple combinations.

None of the soils released P into solution when equilibrated with distilled water. All soils, with the exception of four from the Organ II surface, sorbed all P from the 1- $\mu$ g P/ml solution. Therefore P sorption measured at 10 and at 30  $\mu$ g P/ml ( $X_{10}$  and  $X_{30}$ ) and the PAI at each of these solution supply rates were used as indexes of the sorption capacities of the soils (Table 3). None of these indexes showed a linear or a logarithmic relationship to Fe<sub>o</sub>, Fe<sub>d</sub>, or Al<sub>d</sub>,

TABLE 3

Phosphorus adsorption from 10- $\mu$ g PO<sub>4</sub>-P/ml solutions (X<sub>10</sub>) and 30- $\mu$ g PO<sub>4</sub>-P/ml solutions (X<sub>30</sub>), and phosphorus adsorption indexes from 10-(PAI<sub>10</sub>) and 30-(PAI<sub>30</sub>)  $\mu$ g PO<sub>4</sub>-P/ml solutions in soils from four geomorphic units<sup>a</sup>

	Horizon	X <sub>10</sub> , μg/g	X <sub>30</sub> , μg/g	PAI <sub>10</sub>	$PAI_{30}$
Organ II	A	23.9 (1.8)	34.1 (3.8)	2.7 (0.2)	3.4 (0.04)
J	$8-20~\mathrm{cm}$	27.9 (2.0)	45.6 (2.3)	3.1 (0.2)	4.5 (0.2)
	20-30	33.0 (3.1)	65.3 (3.2)	3.7(0.7)	6.5(0.3)
	30-45	26.5 (2.7)	51.4 (3.3)	2.9 (0.3)	5.1 (0.03)
	45-60	27.6 (0.08)	45.6 (1.6)	3.1(0.1)	4.5 (0.2)
	60-100	33.9 (2.4)	53.9 (7.8)	3.8 (0.3)	5.4 (0.8)
Organ I	A	45.3 (1.3)	73.5 (6.2)	5.2 (0.2)	7.4 (0.6)
6	B1t	49.9 (2.0)	93.2 (9.3)	5.8 (0.3)	9.5 (1.0)
	B2k	78.2 (1.2)	161.9 (4.9)	10.0 (0.01)	17.2 (0.6)
	B3k	76.6 (4.5)	113.1 (3.9)	9.6 (0.7)	11.8 (4.1)
Isaack's Ranch	A	45.2 (0.7)	70.5 (9.3)	5.2 (0.1)	7.1 (1.0)
	B1t	46.6 (0.03)	93.2 (4.1)	5.4 (0.01)	9.4(0.4)
	B2k	60.6 (4.9)	135.6 (5.7)	7.3 (0.7)	14.1 (0.6)
	B3k	52.0 (0.4)	106.8 (4.3)	6.1 (0.2)	10.9 (1.2)
Jornada II	A	49.8 (1.8)	101.9 (14.9)	5.8 (0.2)	10.4 (1.6)
	B1t	57.4 (3.3)	104.9 (2.7)	6.8(0.4)	10.7(0.3)
	B2k	63.4 (6.3)	119.6 (13.7)	7.7(0.9)	12.4 (1.5)
	B3k	69.9 (1.5)	141.1 (6.7)	8.7 (0.3)	14.8 (0.8)
	B4k	89.6 (1.7)	222.8 (4.8)	12.6 (0.5)	25.8 (0.9)

<sup>&</sup>lt;sup>a</sup> Values are means of n = 5 (SE).

either alone or in multiple correlations. All indexes were significantly correlated with the  $CaCO_3$  content of the soils at p < 0.0001 (Figs 2, 3).  $PAI_{10}$  and  $PAI_{30}$  demonstrated the highest linear correlations with percentage of  $CaCO_3$ 

$$PAI_{10} = 0.392 * CaCO_3 + 5.232$$
  $(r = 0.84)$ 

$$PAI_{30} = 0.839 * CaCO_3 + 8.189$$
  $(r = 0.85)$ 

Absolute adsorption capacities ( $X_{10}$  and  $X_{30}$ ) were also significantly correlated with CaCO<sub>3</sub> content, but had better fits to log(CaCO<sub>3</sub>)

$$X_{10} = 19.583 * \log(\text{CaCO}_3) + 56.270$$

$$(r = 0.79)$$

$$X_{30} = 53.462 * \log(\text{CaCO}_3) + 112.339$$

$$(r = 0.80)$$

Adding Fe<sub>o</sub>, Fe<sub>d</sub>, or Al<sub>d</sub> in multiple regressions did not improve these fits. In all cases, correlations were significantly stronger when only those soils that had significantly measurable amounts of  $CaCO_3$  ( $\geq 1\%$   $CaCO_3$ ) were included, and all indexes were most highly correlated with  $log(CaCO_3)$ 

$$X_{10} = 32.220 * \log(\text{CaCO}_3) + 49.842$$

$$(r = 0.91)$$

$$X_{30} = 110.322 * \log(\text{CaCO}_3) + 73.550$$

(r = 0.88)

$$PAI_{10} = 6.119 * log(CaCO_3) + 4.979$$

$$(r = 0.95)$$

$$PAI_{30} = 14.349 * log(CaCO_3) + 6.241$$

$$(r = 0.89)$$

Even when those soils without a significantly measurable level of carbonate (<1% CaCO<sub>3</sub>) were analyzed separately, none of the sorption indexes were correlated with Fe<sub>o</sub>, Fe<sub>d</sub>, Al<sub>d</sub>, or percentage of organic C, either alone or in multiple correlations.

# DISCUSSION

The ratio of Fe<sub>o</sub>:Fe<sub>d</sub> can be used as a measure of the increasing crystallinity of oxyhydroxides during pedogenic development (Alexander 1974; Evans and Cameron 1979; McFadden).<sup>4</sup> In a series of soil chronosequences from xeric to arid climates in southern California, McFadden

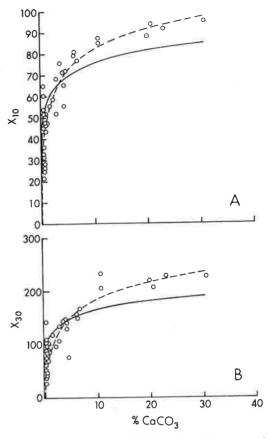


FIG. 2. Correlations between the percentage of  $CaCO_3$  and (A) P adsorption ( $\mu$ g P/g soil) at 10  $\mu$ g P/ml ( $X_{10}$ ) and (B) at 30  $\mu$ g P/ml ( $X_{30}$ ). Solid lines indicate best fit regressions performed using all data points; broken lines indicate best fit regressions performed using only soils where percentage of  $CaCO_3 \ge 1.0\%$ .

found that the Fe<sub>o</sub>:Fe<sub>d</sub> ratio reached a maximum in Holocene to late Pleistocene soils and then decreased in Pleistocene-Pliocene soils as the easily weathered mafic minerals were depleted and paracrystalline ferrihydrite was transformed into hematite.<sup>4</sup> In soils of this study, however, both Fe<sub>o</sub> and Fe<sub>d</sub> continued to increase with increasing soil age through recent Pleistocene soils, and thus there was not a significant shift in the crystallinity of Fe oxyhydroxides—and thus the sorption reactivity—with time.

It was initially suggested that semiarid to arid soils might differ from calcareous soils developed in more humid climates by being pedogenically younger than mesic soils of a similar chronological age and thus might have a lower

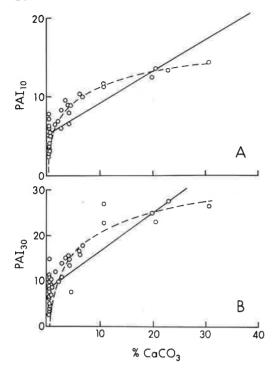


FIG. 3. Correlations between CaCO<sub>3</sub> and phosphorus adsorption index at (A) 10  $\mu$ g P/ml and (B) 30  $\mu$ g P/ml. Solid lines indicate best fit regressions performed using all data points; broken lines indicate best fit regressions performed using only soils where percentage of CaCO<sub>3</sub>  $\geq$  1.0%.

oxyhydroxide content. Although clay mineral authigenesis appears to be relatively limited in arid soils, these soils are subject to and affected by aeolian processes to a larger degree than mesic soils and thus are more likely to contain significant amounts of externally derived oxyhydroxides.4 The range and mean of Fed values in soils of this study were similar, although at the lower end of the range reported in surface soils derived from limestone in Britain (Holford and Mattingly 1975b); both Fe, and Fed were well within the range measured in calcareous soils from Lebanon (Ryan et al. 1985), suggesting that differences in sorption characteristics among these studies are unlikely to be due to large differences in total oxyhydroxide content.

The strong correlation between P adsorption and soil CaCO<sub>3</sub> content found in this study is consistent with soil P fractionation patterns observed previously in these soils (Lajtha and Schlesinger 1988), namely, that over 50% of the total P content of these soils is in a Ca-P bound

form. However, results from this study differ sharply from those of Ryan et al. (1985) and Holford and Mattingly (1975b). Perhaps this difference can be ascribed to the fact that these earlier studies were of surface soils derived from linestone parent material, whereas the source of CaCO<sub>3</sub> in the soils of the present study is aeolian. In their soils derived from Jurassic limestone, Holford and Mattingly (1975c) demonstrated that the specific surface areas of the carbonate component were an inverse function of the percentages of CaCO3 that they contained; the more weathered the soil, the lower the percentage of CaCO<sub>3</sub>, the smaller the particle size, and thus the larger the specific surface area. As sorption should be more directly related to the surfaced area of the reactive fraction of soils than to the total content, it is not surprising that authors have not found a relationship between CaCO3 content and P sorption, even in calcareous soils. In soils where CaCO3 is from aeolian dust, one would not expect such an inverse relationship between CaCO<sub>3</sub> surface area and content. Indeed, it is quite likely for all soils in an arid environment to undergo periodic cyclic dissolution and reprecipitation to form small, high-surface-area CaCO3 grains that would be highly reactive, independent of pedogenic age.

The relationship between P sorption and percentage of CaCO<sub>3</sub> appears to have broad ecosystem implications for the retention of P, both within the soil profile and within the landscape. Total P decreased with increasing soil age over the chronosequence, presumably due to weathering and leaching losses. However, in the three oldest soil geomorphic surfaces with well-defined profile development, total P increased in the lowest, calcic soil horizons relative to midprofile horizons, suggesting a secondary precipitation of Ca-P minerals or strong sorption reactions of P with CaCO<sub>3</sub>. Such reactions could potentially reduce leaching losses of P from the ecosystem. In contrast, total P was lowest in those horizons with the highest levels of Fe and Al oxyhydroxides, suggesting that oxyhydroxides are not significant geochemical agents capable of P retention within this system.

Soils of humid or tropical forests, rich in free Fe and Al oxyhydroxides and sesquioxides, tend to have high P-fixing capacities that render P very immobile. Soil horizons in forested Spodosols with high concentrations of free Al and Fe have been shown to represent zones of strong geochemical fixation that effectively control losses of P to stream water (Wood et al. 1984). In this chronosequence of Aridisols from southern New Mexico, pedogenic CaCO<sub>3</sub> was found to have a higher capacity for P adsorption than Fe or Al oxyhydroxides, and thus CaCO<sub>3</sub> appears to be the primary geochemical agent capable of fixation and retention of P in this ecosystem.

#### ACKNOWLEDGMENTS

This study was performed at the Jornada LTER site of New Mexico State University. We thank William H. Schlesinger and Walter G. Whitford for assistance with all stages of this research. Supported by NSF grants BSR-8413986 (to K.L.) and BSR-8114466 (to the Jornada LTER).

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