

The phosphorus concentration of common rocks—a potential driver of ecosystem P status

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Abstract

Background Soil phosphorus (P) availability can be an important regulator of ecosystem processes. Changes in P availability over time have long been studied, but the P concentration of soil parent materials—which determines ecosystem P concentration at the onset of soil formation—have never been systematically explored. Here we ask two questions: 1) how does P concentration vary among soil parent materials? and 2) under what range of conditions do those differences influence soil P concentration?

Methods We used the Earthchem webportal to compile the P concentration of 263,539 rocks. We then gathered data from 62 sites (MAT ranging from 200–5,000 mmyr⁻¹ and soil age from 0.3–4,100 ky) and assessed the correlation between rock and soil P concentration.

Results We found a 30 fold difference in median P concentration among rock types, ranging from 120 ppm (several ultramafic rocks) to >3,000 ppm

(several alkali basalts). Median P was significantly lower in common silica-rich rocks (e.g. granite - 436 ppm) and higher in common iron-rich rocks (e.g. andesite - 1,000 ppm). In sedimentary rocks, which make up 70 % of the ice-free land surface, median P was highest in mudstone (1,135 ppm) and decreased with increasing grain size (siltstone-698 ppm, sandstone-500 ppm). Where soil P and parent material P were measured in the same site, parent material P explained 42 % of the variance in total soil P ($n=62$), and explanatory power was higher for sites with similar climate.

Conclusion The variation in P concentration among common rock types is on a comparable scale to the changes in total P, and several P pools, over long-term soil development. Quantifying these differences may be an important step towards characterizing regional and global variation in soil and ecosystem P status.

Keywords Phosphorus · Parent material · Bedrock · Nutrient · EarthChem

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Introduction

Phosphorus (P) availability in terrestrial ecosystems can regulate several important processes including primary production (Vitousek 2004; Elser et al. 2007), decomposition (Cleveland et al. 2006) and nitrogen fixation (Vitousek and Howarth 1991). Phosphorus deficiency can arise for several reasons

including: leaching of P over time (Walker and Syers 1976; Vitousek 2004), high water flux through soil (Porder and Chadwick 2009), accumulation of P in recalcitrant minerals or water-logged organic matter (Lajtha and Schlesinger 1988; Vitousek et al. 2010), and formation of barriers to root exploration within a soil profile (Jenny et al. 1969; Lohse and Dietrich 2005). The latter is most common in areas with geomorphic stability that lessen denudation-driven rejuvenation of rock-derived nutrient inputs (Porder et al. 2007b; Porder and Hilley 2011).

Regardless of the processes that drive declines in soil P concentration or the fraction of soil P that is available to plants over a given timescale (Cross and Schlesinger 1995; Johnson et al. 2003), the starting point for the P supply to all soils is the substrate from which it is derived (Jenny 1941; Walker and Syers 1976). Since Walker and Syers's (1976) conceptualization of the relationship between soil P and soil age, there has been intensive study of how phosphorus concentrations and forms change over time (Stevens 1968; Lajtha and Schlesinger 1988; Crews et al. 1995; Selmants and Hart 2010). Surprisingly, there has been little investigation of how the concentration of phosphorus at time=0 (the P concentration of the parent material) varies among ecosystems. Yet this variation may influence the size of all P pools even as they continue to change over time.

Phosphorus in rocks is contained almost wholly in apatite group minerals, and "average" continental crust is typically assumed to contain ~700ppm P (Taylor and McClennan 1985; Okin et al. 2004), though to our knowledge this number has never been rigorously quantified. It makes sense that in young soils, parent material P should influence total soil P. However even under several meters per year rainfall, P depletion of soil can take hundreds of thousands of years (Porder and Chadwick 2009). Thus parent material differences in P concentration may influence ecosystem P availability across broad swaths of the planet where P residence times may be on a similar timescale (Porder and Hilley 2011).

Prior to the work presented here, there have been several studies linking rock P concentration to differences in soil P availability, though in many cases the P concentration of parent rock was assumed rather than measured. In the sub-tropical wet forests of the Atherton Tablelands of Australia, basalt-derived soils have ~6x higher total P concentrations than schist-

derived soils (Gleason et al. 2009), though to our knowledge the P concentrations of the rocks were not analyzed. Low P availability in the South African fynbos soils results from their low P parent material (Soderberg and Compton 2007). The lowest P soils of Mt. Kinabalu, Borneo, are derived from ultramafic rocks which are typically low P (Takyu et al. 2002), and differences between ultramafic and sandstone parent material persists under ~3 m yr⁻¹ rainfall. Similarly, Barro Colorado Island in Panama receives ~2.6 myr⁻¹ rainfall, yet a 3x difference in P concentration persists between soils derived from marine sedimentary rocks and those derived from andesite (Dieter et al. 2010). Under even wetter conditions (3–4 myr⁻¹ MAP) in the Luquillo mountains of Puerto Rico, total soil P on volcanoclastic-derived soils is double that of those derived from quartz-diorite, similar to the 2x difference between the parent materials (Mage and Porder *in press*).

These data suggest parent material P can have an effect on total soil P, and raises the question of the extent to which parent materials differ in their P concentration. We used the EarthChem webportal (<http://www.earthchem.org/>) to address this question. This portal compiles rock analyses (major and trace elements, isotopic composition) from several databases, including: The North American Volcanic and Intrusive Rock Database (NAVDAT), the United States Geological Survey (USGS), Petrological Database of the Ocean Floor (PetDB), Geochemistry of Rocks of the Oceans and Continents (GEOROC), Integrated Data Management for Sediment Geochemistry (SedDB), and a Database for Metamorphic Petrology (MetPetDb). Using these data, we ask how much P concentration varies among common rocks found on the terrestrial surface.

Variation in P concentration among parent materials only matters ecologically if the variation translates into differences in soil P cycling and availability. While the evidence presented above suggests that such links may exist, we wanted to systematically explore the range of climatic conditions and soil age in which parent material P might explain variation in soil P concentration. Thus we gathered data (both published and unpublished) from 62 sites for which both parent material and total soil P had been measured. We assessed the conditions under which these two values are correlated, and under what conditions this correlations break down. Finally, we discuss the extent to which total soil P may or may not be correlated with biologically-relevant P pools.

Methods

Data

We accessed whole-rock analyses from the Earthchem webportal (www.earthchem.org). Rocks in the EarthChem database can be assigned names in a variety of ways, we chose the names assigned to the rocks by the original author. For the analyses presented here, we chose only rock types with at least 200 analyses of P. We excluded rocks for which the name told very little about composition (e.g. tuff, which is volcanic ash but does not specify the composition of the lava) and those that were ambiguous (e.g. greenstone, which can be used to describe several different types of rocks). There were also categories, such as basalt, for which the database contained a generic group (e.g. basalt) and then several subgroups (e.g. alkali basalt, hawaiite, trachybasalt). We analyzed all these groups separately, and discuss their differences below. We chose to leave in sedimentary rock types that do not by definition contain compositional information (e.g. mudstone, sandstone, conglomerate) because particle size in sedimentary rocks can be correlated with composition (Boggs 1987). We also excluded phosphorite (ore-grade P-bearing rock) since the P concentration of this group is well known, and excluded any rocks that have greater than 10 % P_2O_5 (~43,640 ppm) because those could be considered phosphate ore as well. We made the following name changes to rock types from the data from EarthChem: we labeled monzogranite as granite, and chalk as carbonate, since in both these cases the former is a subset of the latter. We also renamed dolerite as diabase and argillite as mudstone since these names are interchangeable. We renamed greywacke as graywacke, and volcanoclastics as volcanoclastic to have consistent spelling throughout the data set. Some rocks in the dataset did not have precise measurements but rather entries of the form "<0.05". We excluded such measurements from analysis.

The gold standard for whole-rock digestion and analysis of rock P concentration is lithium metaborate flux fusion digestion and analysis by XRF, which typically can measure P concentrations as low as 10 ppm reproducibly. However, in the EarthChem database, most of the rock types had at least some reported P concentrations (typically a few percent) that were orders of magnitude lower than this detection limit. We assumed that these values were spurious,

and imposed a lower cutoff of 1 ppm on the data to remove these values before calculating descriptive statistics for each rock type, or statistically comparing their P concentrations. These criteria left us 263,539 analyses of rock P concentration distributed across 69 rock types (Table 1).

Rock groupings

In addition to analyzing each rock type separately, we grouped rock types into the following categories based on Suchet et al. (2003) and Dürr et al. (2005): 1) shield rocks 2) acid volcanic rocks 3) mafic rocks 4) sandstone 5) shale and 6) carbonate (hereafter referred to as "Suchet classes"). We also included ultramafic rocks, not because they are widespread, but because they typically host unique floral communities and have thus attracted ecological investigations greater than their abundance would otherwise suggest (Huenneke et al. 1990; Hooper and Vitousek 1998). The demarcation of individual rock types into these groups can be found in Table 1. Where rocks did not obviously fit into these categories we left them out of these groupings in all statistical analyses (listed as Class=na in Table 1). This analysis is thus weighted towards abundant rocks in the database, which may or may not reflect their abundance on the Earth's terrestrial surface (in an extreme case, there are 97,895 P analyses for "basalt" and 3,207 for "basaltic-andesite", both of which are lumped into "Basalt" as one of seven Suchet classes). At the moment the relative abundance of individual rocks types has not been mapped at the global scale, so it was not possible to weight the P analyses by a measurement of abundance.

Statistical comparisons

None of the data within a rock type, or within the lumped classes above, were normally distributed. They were typically underdispersed and right skewed such that, for almost all rock types, the mode was lower than the median which in turn was lower than the mean. Thus we chose to make comparisons among the classes listed above non-parametrically, using a Kruskal-Wallis test for differences among all Suchet classes, followed by pairwise comparisons with Wilcoxon rank sum tests test (adjusting *p*-values for multiple comparisons). The sample sizes among classes vary widely. To test whether this affected our

Table 1 Descriptive statistics for rock types in the EarthChem database for which there were >200 values after data filtering as described in the methods

Rock name	# in database	Minimum value	25th % ile	Median	Mean	Mode	75th % ile	Class	Alkalic
MONZONITE	2627	44	393	700	946	262	1266	Shield	Y
BASALT	97895	13	567	916	1304	611	1615	Basalt	N
ANDESITE	30711	44	698	1000	1150	873	1396	Basalt	N
GRANODIORITE	6984	44	480	698	810	611	1004	Shield	N
BASALTIC-ANDESITE	3207	87	1091	1440	1551	1440	1789	Basalt	N
RHYOLITE	14194	10	131	305	493	87	524	Acid Volcanic	N
DACITE	9751	44	567	742	844	611	1004	Acid Volcanic	N
GRANITE	7740	22	262	436	568	436	700	Shield	N
SYENITE	1338	44	349	786	1195	262	1527	Shield	Y
DIORITE	4407	44	698	1004	1262	873	1527	Shield	N
GABBRO	6041	15	218	524	962	87	1047	Basalt	N
TRACHYTE	3917	44	349	611	851	349	1091	Shield	Y
TRACHYANDESITE	1586	44	1396	2095	2360	1920	2968	Basalt	Y
LATITE	2063	44	567	1004	1226	524	1615	Acid Volcanic	Y
MONZOGRANITE	548	44	175	349	445	262	652	Shield	N
TONALITE	1307	44	524	698	803	611	1004	Shield	N
APLITE	370	22	131	262	991	87	524	Shield	N
THOLEIITE	10322	44	655	999	1021	1004	1178	Basalt	N
RHYODACITE	1233	44	393	567	695	436	829	Acid Volcanic	N
MUGEARITE	730	175	2487	3360	3534	2793	4364	Basalt	N
SHOSHONITE	728	87	1440	1964	2087	1877	2531	Basalt	Y
PHONOLITE	1860	44	262	698	1223	175	1615	na	na
ANKARAMITE	367	87	1222	1789	2176	1091	2645	Basalt	N
DIABASE	5036	44	480	698	1049	611	1178	Basalt	N
HAWAIIITE	1970	175	2313	3055	3294	2706	3928	Basalt	Y
LAMPROPHYRE	634	131	1789	2946	3501	1877	4539	na	na
COMENDITE	221	22	87	131	250	87	262	Acid Volcanic	N
BENMOREITE	364	131	1266	2138	2382	1702	2793	Basalt	Y
BASANITE	2735	44	2531	3229	3465	2706	4146	na	na
PEGMATITE	230	44	262	500	1003	400	900	na	na
MINETTE	238	1135	2400	3775	3936	5717	5542	na	na
TRACHYBASALT	1547	305	1964	2531	2911	1920	3666	Basalt	Y
CARBONATITE	687	44	1737	4757	6978	7000	10000	na	na
MONZODIORITE	289	80	873	1309	1622	786	2051	Shield	N
NEPHELINITE	980	131	3011	4015	4515	3622	5346	Basalt	na
KIMBERLITE	2485	44	1571	1877	2006	1877	2266	na	na
PERIDOTITE	577	13	45	131	422	44	292	Ultramafic	N
PANTELLERITE	267	44	87	175	245	87	218	Acid Volcanic	Y
PYROXENITE	535	21	131	262	1463	87	644	Ultramafic	N
TEPHRITE	621	175	2226	3186	3380	2575	4233	na	na
PICRITE	1404	44	393	698	933	655	1135	Basalt	N
ADAKITE	391	92	439	786	881	349	1165	na	na
LEUCITITE	315	480	1785	2357	2759	2968	3120	na	na
DUNITE	200	13	44	131	309	44	249	Ultramafic	N

Table 1 (continued)

Rock name	# in database	Minimum value	25th % ile	Median	Mean	Mode	75th % ile	Class	Alkalic
BONINITE	395	25	131	181	302	175	305	Basalt	na
PHONOTEPHRITE	237	305	2487	3229	3327	3229	4015	na	na
KOMATIITE	1955	13	87	131	246	87	262	Ultramafic	N
GNEISS	2603	44	305	567	867	262	960	Shield	na
META-BASALT	591	44	480	742	911	436	1135	Basalt	na
AMPHIBOLITE	1156	44	436	655	974	436	1100	Basalt	na
QUARTZITE	435	13	200	393	604	300	611	Shield	na
SCHIST	1689	44	436	655	910	611	1000	Shield	na
SLATE	656	50	349	600	754	300	829	Shield	na
PHYLLITE	358	50	436	655	905	567	900	Shield	na
CHERT	506	50	300	400	1597	349	900	na	na
CARBONATE	2253	10	178	289	395	300	425	Carbonate	na
MUDSTONE	2083	13	600	1135	5159	300	5000	Shale	na
SILTSTONE	1684	50	393	698	2829	500	1309	Shale	na
CONGLOMERATE	366	60	300	600	1191	200	1100	Sandstone	na
SANDSTONE	4610	10	262	500	1127	200	900	Sandstone	na
CLAYSTONE	469	44	400	700	2797	873	1309	Shale	na
LIMESTONE	2095	11	218	500	1560	200	1266	Carbonate	na
DOLOMITE	291	44	175	567	2844	87	1900	Carbonate	na
OIL SHALE	711	50	700	1047	1627	700	1795	na	na
BIOGENIC	1216	44	393	520	616	400	698	na	na
SILICICLASTIC	3468	40	450	698	1549	524	1251	na	na
METALIFEROUS	1048	110	6900	10000	12289	10600	11500	na	na

statistical comparisons, we generated 10,000 bootstrap replicates where 1,000 P measurements were drawn with replacement from each Suchet class and conducted a Kruskal-Wallis test for each bootstrap replicate. We then conducted pairwise Wilcoxon tests comparing the location of the distributions of P measurements between each pair of Suchet classes. Again, 10,000 replicates were drawn with 1,000 measurements sampled with replacement from each rock type (these resamples were different from the Kruskal-Wallis resamples). We present the mean *p*-value observed for each pair across these 10,000 replicates, as well as the 95 % credibility interval for these *p*-values, corrected for multiple comparisons.

Effect sizes

Given the number of samples in any given rock type (always >200 and often >1,000), and the even higher

number of samples in our broad groupings (e.g. shield, basalt, etc.), statistically differences among rock types do not necessarily translate to ecologically and biogeochemically relevant differences across lithologic contacts. Thus we used Cohen's *f* as a measure of the effect size of the difference in P concentration between our six rock groups. Cohen's *f* is an effect size measure used in the context of analysis of variance, as a complement to the parametric F-test in ANOVA, and is calculated as:

$$\hat{f} = \frac{\bar{x}_1 - \bar{x}_2}{\sqrt{\frac{(n_1-1)s_1^2 + (n_2-1)s_2^2}{n_1+n_2}}} \quad (1)$$

where n_i is the sample size of rock type *i* in this analysis of P measurements, \bar{x}_i is the mean P concentration of rock type *i* and s_i^2 is the sample variance of P concentration for rock type *i*. Although admittedly subjective, a Cohen's *f* > 0.4 is considered a large effect size, 0.1–0.4 a

moderate effect size, and <0.1 a small effect size (Sokal and Rohlf 2011).

The link between rock P and soil P

In order to assess whether rock P concentration translates to total soil P concentration we gathered data from 62 sites where we (or others) have measured soil P (0–50 cm) and parent material P. Samples described as “unpublished data” (Table 2) were sampled from soil pits to a depth of 50 cm, air dried, and analyzed for total elements by lithium metaborate flux fusion followed by XRF at ALS Chemex (Sparks, Nevada). This method has a detection limit of 10 ppm for P. Soil sampling protocols and determination of parent material for samples from Hawai’i follow Chadwick et al. (2003) and Porder et al. (2007a). Briefly, for Hawaiian soils on the Big Island parent material was determined by digging with shovels, or with a backhoe, to bedrock, which was considered soil parent material. For other locations (Molokai, Kauai, Puerto Rico, Guatemala, Brazil, Taiwan) parent material was assessed from rocks collected on landslide scars near the soil pits or from streams draining the sites. Soil data presented here are depth-weighted averages to a depth of 50 cm. Parent materials ranged from granites to basalts, from 200–5,000 mm yr^{-1} in rainfall and from 300–4.1 million years in soil age (Table 2). Forty-four of these sites are in the Hawai’ian Islands, but typical of the global dataset, there is substantial variation in P concentration among individual lava flows (Table 2).

All statistical analyses were done using R (version 2.14.1)

Results

Overall, we found large differences in total P between most rock types, despite large variance within a rock type (Table 1). Within igneous rocks, P increases from silica-rich, iron-poor, rocks such as granite (median P=440 ppm) and rhyolite (median P=310 ppm) to intermediate rocks such as andesite (median P=1,000 ppm) and iron-rich, silica-poor, rocks such as basalt (median P=920 ppm; Table 1). Within the intermediate and iron-rich rocks, alkali concentration is strongly associated with high P. Alkali basalts, trachybasalts and trachyandesite (both alkali-feldspar rich), all have median P>2,000 ppm. In contrast, tholeiitic

basalts (which make up the basalts of the ocean floor and are low in alkalis) have median P=1,000 ppm, as does the undifferentiated “basalt” category in EarthChem, which is dominated by ocean-floor tholeiites (K. Lehnert, pers. comm.). Among the igneous rocks, and indeed across all rock types, ultramafic rocks such as peridotite (median P=120 ppm) and pyroxenite (median P=260 ppm) have the lowest P.

Sedimentary rocks show a pronounced decrease in P concentration with increasing grain size. Mudstone, claystone and siltstone (median P=1,100, 700, 698, respectively) have higher P than sandstone and conglomerate (median P=500 and 600 ppm, respectively). Limestone and dolomite have similar P concentrations to sandstones, though the category “carbonate” has much lower P (median 290 ppm), which may reflect the inclusion of mixed siliciclastic-carbonate rocks in this generic class.

Overall, metamorphic rocks contain similar amounts of P to their sedimentary and igneous precursors. Metamorphosed mud and claystones such as slate, phyllite and schist have similar median P (570–660 ppm), and while “schist” does not necessarily imply a sedimentary protolith, the majority of schists are derived from similar parent material as phyllite and slate (Spear 1993). In contrast, gneiss can result from the metamorphism of several different protoliths (though most commonly it is granitic in composition), and similar to granite, gneiss has a median P (567 ppm) lower than most metamorphic or sedimentary rocks. Not surprisingly, metamorphosed ultramafic rocks such as serpentinite, a substrate that has received a great deal of interest because it often hosts native flora in heavily invaded grasslands (Huenneke et al. 1990) and unique flora generally (Proctor 2003), has the lowest P of any rock type analyzed (90 ppm), but this number is based on only 19 analyses in the database and is not shown in Table 1.

Regardless of their origin, all rock types showed substantial variation in P concentration within a type, typically several hundred ppm or more. For example, the interquartile range in granite spanned 260–700 ppm, and in schist from 440–1,000 ppm. Nevertheless, when rocks were grouped into broad categories such as “shield” and “mafic” we found highly significant differences among most categories (Figure 1). Bootstrap results suggest the only comparisons between rock types that were not significant at $p < 10^{-5}$ were between acid volcanics and sandstone, acid volcanics and carbonate

Table 2 Soil P concentration (0-50 cm) and the P concentration of parent material at 62 sites for which both these values have been measured, along with soil age and precipitation at those sites. Data sources are: 1) Porder and Chadwick 2009, 2) Mage

and Porder (in press), 3) S. Porder, unpubl. data, 4) Chadwick et al. 1999 and O.A. Chadwick, unpubl. data and 5) O.A. Chadwick, unpubl. data

Site	Location	Soil age ky	Map mm yr ⁻¹	Soil P ppm	Parent P ppm	Citation
Kona	Big Island, Hawai'i	10	640	4517	655	1
Kona	Big Island, Hawai'i	10	990	1266	218	1
Kona	Big Island, Hawai'i	10	1220	2383	611	1
Kona	Big Island, Hawai'i	10	1650	2173	916	1
Kona	Big Island, Hawai'i	10	1700	2182	655	1
Kona	Big Island, Hawai'i	10	1980	2199	524	1
Kona	Big Island, Hawai'i	10	2400	1658	480	1
Hawi	Big Island, Hawai'i	170	160	3414	7419	1
Hawi	Big Island, Hawai'i	170	180	1702	5891	1
Hawi	Big Island, Hawai'i	170	180	594	5891	1
Hawi	Big Island, Hawai'i	170	210	2905	6546	1
Hawi	Big Island, Hawai'i	170	270	2743	5760	1
Hawi	Big Island, Hawai'i	170	570	3578	7244	1
Hawi	Big Island, Hawai'i	170	790	3578	8379	1
Hawi	Big Island, Hawai'i	170	930	6378	8030	1
Hawi	Big Island, Hawai'i	170	1260	11652	7681	1
Hawi	Big Island, Hawai'i	170	1500	9514	7113	1
Hawi	Big Island, Hawai'i	170	1800	5237	7462	1
Hawi	Big Island, Hawai'i	170	2500	3404	9601	1
Pololu	Big Island, Hawai'i	350	180	1396	1440	1
Pololu	Big Island, Hawai'i	350	250	1527	1789	1
Pololu	Big Island, Hawai'i	350	750	2007	2531	1
Pololu	Big Island, Hawai'i	350	900	2313	2138	1
Pololu	Big Island, Hawai'i	350	1000	1440	3884	1
Pololu	Big Island, Hawai'i	350	1100	2357	2138	1
Pololu	Big Island, Hawai'i	350	1200	3928	1571	1
Pololu	Big Island, Hawai'i	350	1300	2852	2269	1
Pololu	Big Island, Hawai'i	350	1500	1353	2138	1
Pololu	Big Island, Hawai'i	350	1800	2074	1571	1
Pololu	Big Island, Hawai'i	350	1900	2618	2138	1
Pololu	Big Island, Hawai'i	350	2000	1287	2269	1
Pololu	Big Island, Hawai'i	350	2100	1309	2269	1
Pololu	Big Island, Hawai'i	350	2400	1113	2007	1
Pololu	Big Island, Hawai'i	350	2500	680	2138	1
TabDys14	El Yunque, Puerto Rico	na	3850	153	260	2
TabDys 15	El Yunque, Puerto Rico	na	3876	196	303	2
TabDys16	El Yunque, Puerto Rico	na	3544	188	310	2
TabOx9	El Yunque, Puerto Rico	na	4013	340	486	2
Tab)x10	El Yunque, Puerto Rico	na	3658	292	488	2
TabOx11	El Yunque, Puerto Rico	na	3882	375	496	2
TabOx12	El Yunque, Puerto Rico	na	3540	271	657	2

Table 2 (continued)

Site	Location	Soil age ky	Map mm yr ⁻¹	Soil P ppm	Parent P ppm	Citation
TabOx13	El Yunque, Puerto Rico	na	3663	432	762	2
BRUB S1-3	Mata Atlantica, Brazil	na	3000	236	480	3
BRUB S6-8	Mata Atlantica, Brazil	na	3000	140	1386	3
BRUB S11-13	Mata Atlantica, Brazil	na	3000	916	1386	3
TW S6-8	Taiwan	na	5000	625	3273	3
TW S19-21	Taiwan	na	5000	451	218	3
TW S24-26	Taiwan	na	5000	320	175	3
GTS 1-3	Sierra De Las Minas, Guatemala	na	3000	148	240	3
Hamaca Ridge	Las Alturas, Costa Rica	na	3500	1456	960	3
Cedro Quarry	Las Alturas, Costa Rica	na	3500	1051	1004	3
Thurston	Big Island, Hawai'i	0.3	2500	916	873	4
LauPahoehoe	Big Island, Hawai'i	20	2500	1964	2182	4
Kohala	Big Island, Hawai'i	150	2500	5586	7812	4
KoleKole	Molokai, Hawai'i	1400	2500	2051	2793	4
Koke'e	Kauai, Hawai'i	4100	2500	1353	1309	4
Wet LSAG 1	Big Island, Hawai'i	0.2	4000	1069	873	5
Wet LSAG 2	Big Island, Hawai'i	6	4000	1127	873	5
Wet LSAG 3	Big Island, Hawai'i	20	4000	1416	1746	5
Wet LSAG 4	Big Island, Hawai'i	150	4000	2122	7812	5
Wet LSAG 5	Maui, Hawai'i	400	4000	690	2357	5
Wet LSAG 6	Molokai, Hawai'i	1400	4000	468	2784	5
Wet LSAG 7	Kauai, Hawaii	4100	4000	1222	1309	5

(the lower bound of the 95 % credibility interval derived from bootstrapping was only $p=0.03$, the mean p -value was 0.0059), and between basalt and shale (Table 3). Iron-rich rocks (dominated by analyses of basalt) had the highest P concentrations (median P concentration 960 ppm) and ultramafics the lowest (median P=165 ppm). Rocks that are even more abundant on Earth's surface also differed significantly in P concentration. Shield rocks had relatively low P (median=650) relative to shale (median=870).

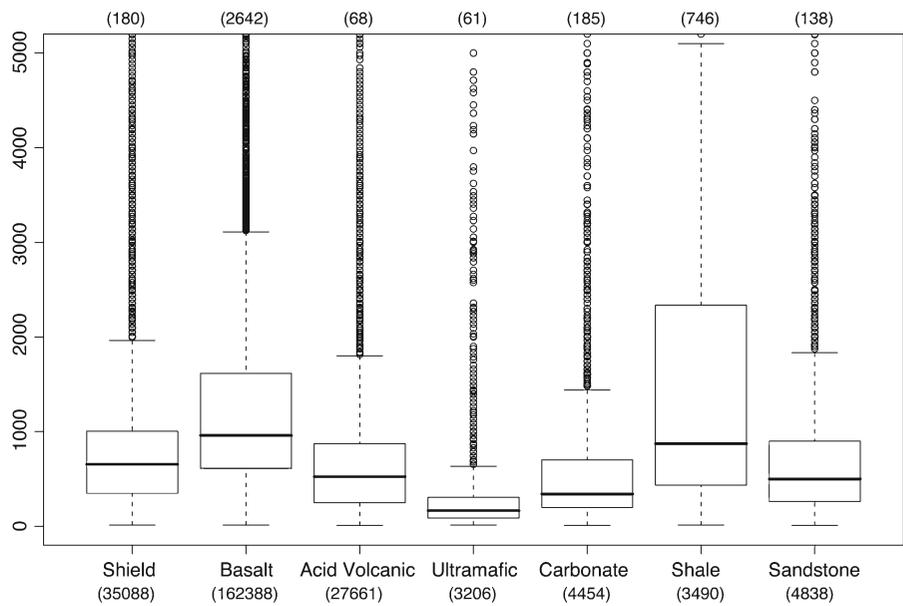
Given the large sample sizes in these analyses, statistically significant differences between rock groups may not correspond to large differences in median P, and thus may not indicate ecologically important contrasts. Thus we explored the differences between rock types for both statistical significance and the size of difference as encapsulated by the Cohen's f statistic (Table 3). In these analyses, P-rich intermediate and iron-rich rocks stand out from the low-P carbonates, granites, and ultramafics.

Our dataset of soil and parent material P concentrations measured in individual sites shows a significant correlation ($N=62$, $r^2=0.42$, $p<0.001$) despite a wide range of variation in soil age, climate, rock type and P concentrations (Table 2, Figure 2). Within this dataset, rock P explains even more variance across sites with similar climates (Figure 2, upper sub-panels). In soils of similar age but with very different climates, rock P concentration explains variance in soil P on young soils (in this case 10 ka), but not on soils that have been exposed to different climatic conditions for a very long time (in this case 350 ka; Figure 2, lower sub-panels).

Discussion

Since the publication of Walker and Syers's (1976) seminal paper the role of soil age in explaining differences in soil P status among sites has been extensively

Fig. 1 Boxplots showing the distribution of P concentrations among seven Suchet classes of rocks. Rock types included in each class are given in Table 1. Parentheses below the rock name show the total number of analyses in each class. For visualization, we chose to limit the y-axis to 5000 ppm. The numbers in parentheses above the graph show the number of points in each rock class with P > 5000 ppm. The points omitted here because of the limited y-axis were included in all analyses (e.g. Tables 1 and 3)



explored (Stevens 1968; Lajtha and Schlesinger 1988; Crews et al. 1995; Selmants and Hart 2010). The vast majority of that exploration has focused on transformations over time, either in total P concentration, or in the shifts in P forms that accompany the long-term decline of P during weathering. Total P may decrease by a factor

of six over hundreds of thousands of years in some settings (Stevens 1968; Oon 1971), more labile forms can change by a factor of almost 15 between P-rich and poor sites along a chronosequence. Interestingly, the variation in the P concentration of common rock types, which can set the actual P concentration in various P

Table 3 a) *p*-values for comparisons between different classes of common parent materials. *p*-values are based on 10,000 bootstrapped samples from each rock class for each pairwise comparison; *p*-values are further corrected for multiple comparisons (i.e., all pairwise comparisons are conducted for each bootstrap replicate). Zero values are given for $p < 10^{-16}$. b) Cohen's *f* comparison between major classes of rocks. A

Cohen's *f* larger than 0.4 (bold) is considered a large difference, from 0.1-0.4 a moderate difference (denoted by italics). Positive Cohen's *f* indicate column value greater than row. Using that definition, note that shield rocks (such as those that underlie the eastern Amazon and Central African rainforests) are very different from the rock types more common in the temperate zone

	Acid Volcanic	Basalt	Carbonate	Sandstone	Shale	Shield
<i>p</i> -values for Kruskal-Wallis determined differences between Suchet Classes						
Basalt	0	-	-	-	-	-
Carbonate	0.0059	0	-	-	-	-
Sandstone	0.85	0	5.8E-05	-	-	-
Shale	0	0.85	0	0	-	-
Shield	3.6E-05	0	0	0.0036	3.6E-10	-
Ultramafic	0	0	0	0	0	0
Cohen's <i>f</i> measuring the magnitude of difference in P concentration between Suchet Classes						
Basalt	-0.27	-	-	-	-	-
Carbonate	-0.15	0.09	-	-	-	-
Sandstone	-0.16	0.07	-0.01	-	-	-
Shale	-0.55	-0.76	-0.25	-0.24	-	-
Shield	-0.09	0.19	0.08	0.10	0.56	-
Ultramafic	0.11	0.34	0.12	0.12	0.29	0.17

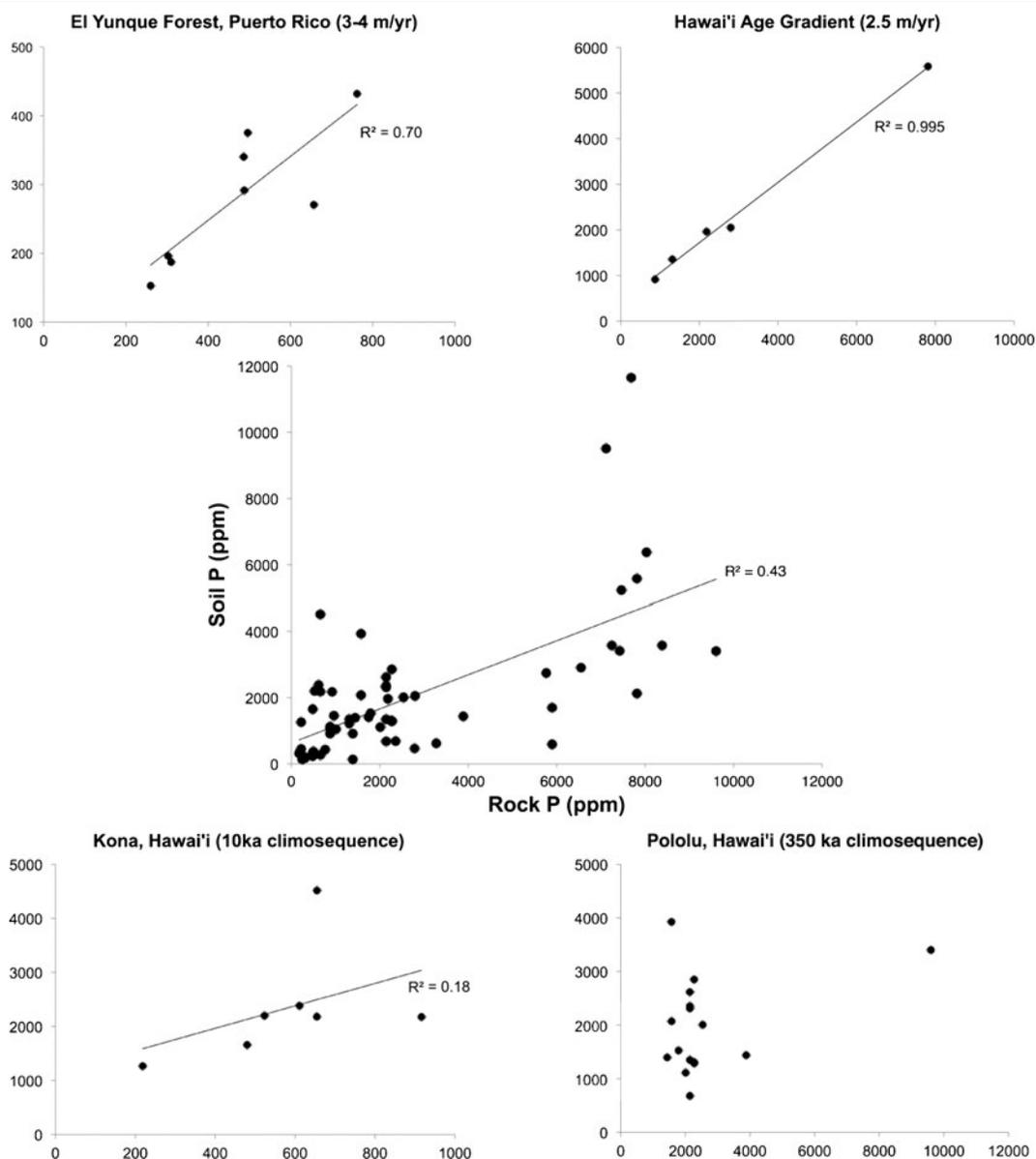


Fig. 2 Soil P plotted against the P concentration of the rocks from which the soil was derived. Note that for regions with similar climate (top two inset panels), rock P is a strong predictor of soil P. In young soils (e.g. 10 ka) rock P does predict soil P (if the high soil P point is considered an outlier and removed $R^2=0.57$ for the Kona climosequence shown on the bottom left panel). In contrast,

rock P is a poor predictor of soil P in older soils that differ greatly in climatic conditions (e.g. the Pololu Climosequence, bottom right panel). Axes on the sub panels are the same as those in the central panel - parent material P on the x-axis and soil P on the y-axis. If R^2 is reported $p < 0.05$ for the regression line

pools, varies by a similar amount (Figure 3). Many authors have suggested that differences in P availability between regions may be a result of differences in soil age (e.g. differences due to sitting at different points on the x-axis in figure 3; Vitousek 1984; Martinelli et al. 1999; Reich and Oleksyn 2004). However it seems

equally possible that such differences could arise from differences in parent material P concentration without invoking soil aging (Porder and Hilley 2011). Quantification of parent material P concentration may help inform our understanding of differences in soil P status across landscapes or among regions.

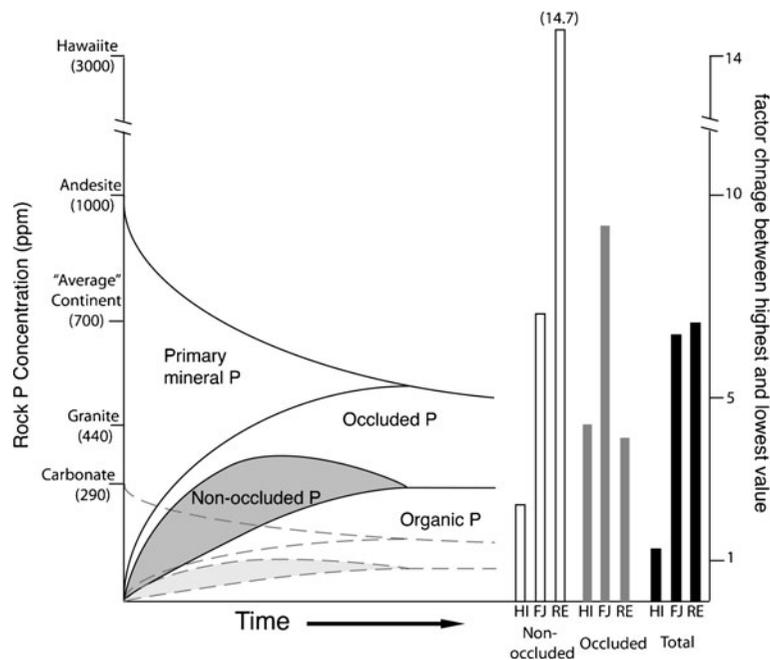


Fig. 3 Changes in P fractions over time as conceptualized by Walker and Syers (1976). The left-hand y-axis plots the median P concentration of several common crustal rocks. The solid lines show the progression of P pools starting at 1000 ppm (andesite parent material), the dashed lines show the identical progression starting at 290 ppm (carbonate parent material). Note this hypothetical difference in starting point produces different-sized P pools, for example the “non-occluded P” pools are highlighted by grey shading. The right hand y-axis shows the factor by which labile P (g m^{-2} , open bars), fraction recalcitrant P (% of total, grey bars) and total P (g m^{-2} , black bars) varies among sites

The descriptive statistics for each rock type present here can be used to generate *a priori* expectations for such differences, particularly for areas that share similar climates. Nevertheless, the variance within rock types necessitates analyses of parent material at the sites in order to refine these expectations. For example, the soils of the Atherton Tablelands in Australia discussed above have 6x higher P on basalt than on schist-derived soils (Gleason et al. 2009). Our analysis suggests a smaller difference among these rock types, and their interquartile range shows substantial overlap (567–1,616 ppm and 436–1,000 ppm for basalt and schist, respectively; Table 1). Analysis of the parent material would allow a more robust interpretation of the drivers of these observed soil differences. In addition, even rocks lumped together on a geologic map of a particular site may have large variation in P concentration. For example, Mage and Porder (in press) found a 2x difference in the mean concentration between

on different chronosequences. For example, non-occluded P varies by a factor of ~2 from the most P-rich to P-poor site along the Hawai’ian chronosequences. Note that differences in parent material produces differences in pool sizes of a similar order of magnitude than those observed over time. Hawai’i (HI) data from Crews et al., (1995), Franz Joseph (FJ) data from Stevens (1968), Reefton (RE) data from Tan (1971). Labile P is defined as NaHCO_3 or NH_4F -extractable plus NaOH extractable P. Occluded P is defined as that which is not extractable by sequential Hedley Fractionation

volcaniclastic (605 ppm, $n=31$) and quartz diorite (300 ppm, $n=20$) gathered across tens of square kilometers in the Luquillo Mountains of Puerto Rico. While analyses of the quartz diorite varied only slightly (260–300 ppm), the volcaniclastics ranged from 288–1,126 ppm. For such highly variable rock types, it is important to analyze multiple samples in order to assess the influence of parent material P on soil P.

Whether or not differences in rock P are relevant to the functioning of soils and ecosystems depends on two questions which bear closer examination: 1) under what set of conditions does parent material P translate into soil total P? and 2) to what extent is total soil P an ecologically relevant parameter? There are many reasons to posit that across the types of gradients we include in our parent material versus soil P analysis (Table 2), rock P would not explain much variance in soil P. It has been well-documented in older soils that exogenous material (dust, sea salt aerosols, organic

matter) can add substantial P to soils relative to what is derived from rock weathering (Kurtz et al. 2001; Porder et al. 2007a; Pett-Ridge 2009). Plants can transfer P from depth to the upper soil (Jobbágy and Jackson 2001), and this phenomenon can result in enrichment of P in upper soils relative to parent material (Porder and Chadwick 2009). Finally, intense weathering over long timescales decouples soil P concentration from that of the parent material as P is increasingly supplied to ecosystems via dust deposition (Walker and Syers 1976; Vitousek 2004). Surprisingly, through all of this noise, parent material P explains 42 % of the variance in soil P across the 62 sites for which we and others have measured both values.

In addition to noting this influence, however, it is worth discussing the conditions under which the coupling breaks down, to inform our expectations as to where we might expect rock P to really matter to ecosystem properties. To explore this, we compared soil P on two Hawaiian lava flows of different ages (Sites: Hawi and Polulu in Table 2) which cross a climate gradient in the Kohala Mountains from ~200–2,500 mm yr⁻¹ rainfall and thus from highly negative to highly positive water balance. The 170 ka flow is alkali basalt with very high P (~6,800 ppm), ~3.4 times that of the 350 ka tholeiitic basalt flow (~2,000 ppm P). Across the climate gradient soil P differs among three climate zones because of non-linear changes in weathering intensity (Chadwick et al. 2003; Porder et al. 2007a) and the uplift and retention of P in the upper soil under mesic climatic conditions (Porder and Chadwick 2009). In dry areas the ratio of soil P: parent material P is less than one (perhaps due to P losses from biomass blowing into the nearby ocean, O.A. Chadwick, pers. comm.). At intermediate rainfall this ratio is much greater than one because of the uplift of nutrients by plants (Porder and Chadwick 2009), and in the wetter sites it falls back below one as a result of intense weathering over long timescales (Chadwick et al. 2003). However, for any given climate zone, the soil P on the Hawi flow is, on average, 2.4x greater on the Hawi flow than on the Polulu flow, similar to the 3.4x difference in parent material (Figure 4).

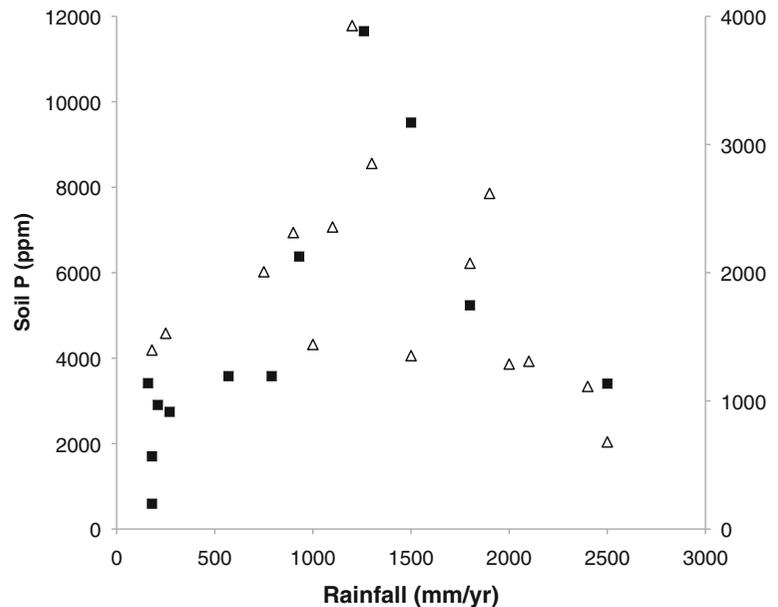
These data suggest a strong influence of parent material P on total soil P, particularly among areas with similar climate. However the relevance of total soil P to the supply of P to ecosystems remains an open question. There is a continuum of P forms in the soil, from rapidly bioavailable orthophosphate in soil

solution to organic and mineral-bound PO₄³⁻ that turns over on substantially longer timescales (Walker and Syers 1976; Cross and Schlesinger 1995; Johnson et al. 2003; Syers et al. 2008; Turner and Engelbrecht 2011). In the almost four decades since Walker and Syers's paper, we have made little progress in measuring these conceptually useful pools, and still can only approximate them with chemical extractions (Hedley et al. 1982; Tiessen and Moir 1993). While our ability to detect different forms of organic P with NMR is growing rapidly (Turner et al. 2007), our understanding of the turnover time (and thus bioavailability) of different organic forms is still in its infancy.

Thus the relationship between total soil P and biologically available P (over whatever timescale) is poor. The most commonly-used assays for "available P" (e.g. acid fluoride (Bray and Kurtz 1945) or bicarbonate extractions (Olsen et al. 1954)) do not correlate well with total soil P (Crews et al. 1995; Gleason et al. 2009). However, there is ample evidence that these "readily-extractable" pools do not adequately describe the P available for plant uptake (Le Bayon et al. 2006; Syers et al. 2008). The more chemically recalcitrant NaOH-extractable pool has been shown to turn over on decadal timescales in regrowing forests (Richter et al. 2006). On the time scale of minutes to days, Fe binding of P, considered a primary driver of P poverty in tropical soils (Sanchez 1976) can be reversed if redox changes promote either the episodic (Chacon et al. 2006b) or prolonged (Miller et al. 2001) Fe reduction.

In contrast to the most labile P forms, measures of organic P do correlate with total soil P across a wide range of concentrations and parent materials (Harrison 1987; Turner 2008; Turner and Engelbrecht 2011). The turnover time of the many forms of organic P is poorly understood, but both mono- and diesters likely can be readily accessed by both plants and mycorrhizal fungi (Turner 2008). In almost all soils organic P represents a very large pool of P relative to biological demand (Johnson et al. 2003). Furthermore, the forms and decomposability of different P compounds varies as soil P declines during soil weathering. For example, myo-inositol hexakisphosphate (a recalcitrant organic P compound) increases in abundance across chronosequences that show total P depletion over time (McDowell et al. 2007). It is unclear whether the increased concentration of recalcitrant P in more highly weathered soils is due to longer turnover time or represents a plant-soil feedback whereby plants

Fig. 4 Variation in soil P concentration (0–50 cm depth weighted by horizon) across two adjacent Hawaiian lava flows, the 170 ka Hawi Flow (black squares, primary y-axis) and the 350 ka Pololu Flow (open triangles, secondary y-axis). The Hawi parent material is 3.4x more P rich than that of the Pololu, similar to the difference in soil P concentration between the flows for a given climate. Note the second y-axis is scaled to 3x lower values than the primary y-axis. Data from Porder and Chadwick 2009



growing on low P parent material produce a larger fraction of recalcitrant P compounds in their tissues (or both). The latter represents a potential feedback between low P parent material and low P fertility that links to the broader concept of reduced soil fertility via increased nutrient use efficiency (Vitousek 1982, 2004). Seen in this light, the correlation between rock P and total soil P becomes part of a chain linking rock to organic to bio-available P that merits additional investigation.

Parent material composition may also influence soil P availability indirectly, because rocks vary widely in other elements, notably iron and aluminum, that interact with P in soils (Sanchez 1976; Peretyazhko and Sposito 2005; Chacon et al. 2006a). In a wet (3–4 myr⁻¹ rainfall) tropical forest in Puerto Rico, Mage and Porder (in press) found that the clayey Oxisols developed on iron-rich volcanoclastic parent material had ~60% of P bound in a recalcitrant pool (defined as not extractable with NaHCO₃, NaOH or HCl), whereas adjacent sandy Dystrudepts developed in the same climate and over similar timescales but derived from iron-poor quartz diorite had ~30% P in this form. In similarly wet conditions, soils derived from sedimentary rocks on Mt. Kinabalu in Borneo had ~30% of their P in occluded form, whereas soils derived from ultramafic rocks in the same locations varied much more from site to site (4–66 %) in their recalcitrant P concentration (Kitayama et al. 2000). On Barro Colorado Island (Panama), soils derived from marine sediments had substantially more

P bound in recalcitrant form than andesite-derived soils (Dieter et al. 2010), despite being found on steeper slopes where the supply of primary mineral P should be rejuvenated (Porder et al. 2005).

To our knowledge, parent material effects on P forms have not been explicitly tested in arid or semi-arid systems. However P in arid soils is commonly bound to pedogenic carbonate, and thus we expect parent material may be a less important driver of P form. Consistent with this expectation, a 2,000 ky basaltic (Fe-rich) chronosequence across the San Francisco volcanic field in Arizona, receiving 340 mmyr⁻¹ rainfall, had ~30% of total P in relatively recalcitrant form (Selmants and Hart 2010), similar to a Fe-poor rhyolitic chronosequence developed under even more arid conditions (160 mmyr⁻¹) at the Jornada Field Station in New Mexico (Lajtha and Schlesinger 1988). Though these data are far from conclusive, they suggest that parent material may be less important than other factors (pedogenic carbonate formation, dust mobilization and deposition) in driving P dynamics in arid ecosystems.

Conclusion

Walker and Syers's (1976) conceptualization of P transformations over time has inspired a great deal of research on the P status of ecosystems in the past three and a half decades. Much of this has focused on the conversion of mineral P to biologically available P to

more recalcitrant P as soils weather (Lajtha and Schlesinger 1988; Crews et al. 1995; Selmants and Hart 2010). With data from well-dated chronosequences, much progress has been made in understanding the timescales over which these P transformations occur. It takes $\sim 1,000$ ky to drive down P availability on Hawaiian basalts under $2,500 \text{ mmyr}^{-1}$ rainfall, but only 100 ky to do so on New Zealand till under slightly wetter conditions (Porder et al. 2007b). But much less attention has been paid to the P-concentration axis, which sets the stage for the total amount of P in each form in the soil profile even as it evolves. Our review suggests this axis matters, and merits additional investigation as comparisons are made between sites. Given this, we suggest that the link between rock, total soil, organic, and biologically-available P should be a focus of P-related ecosystem research in the coming decade. This may be a way forward in the heretofore difficult task of *a priori* predicting the P status of terrestrial ecosystems.

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References

- Boggs S Jr (1987) Principles of sedimentology and stratigraphy. Macmillan Publishing Co., New York, p 784
- Bray RH, Kurtz LT (1945) Determination of total, organic, and available forms of phosphorus in soils. *Soil Sci* 59:39–45
- Chacon N, Flores S, Gonzalez A (2006a) Implications of iron solubilization on soil phosphorus release in seasonally flooded forests of the lower Orinoco River, Venezuela. *Soil Biol Biochem* 38:1494–1499
- Chacon N, Silver W, Dubinsky E, Cusack D (2006b) Iron reduction and soil phosphorus solubilization in humid tropical forests soils: the roles of labile carbon pools and an electron shuttle compound. *Biogeochemistry* 78:67–84
- Chadwick OA, Derry LA, Vitousek PM, Huebert BJ, Hedin LO (1999) Changing sources of nutrients during four million years of ecosystem development. *Nature* 397:491–497
- Chadwick OA, Gavenda RT, Kelly EF, Ziegler K, Olson CG, Elliott WC, Hendricks DM (2003) The impact of climate on the biogeochemical functioning of volcanic soils. *Chem Geol* 202:195–223
- Cleveland CC, Reed SC, Townsend AR (2006) Nutrient regulation of organic matter decomposition in a tropical rain forest. *Ecology* 87:492–503
- Crews TE, Kitayama K, Fownes JH, Riley RH, Herbert DA, Mueller-Dombois D, Vitousek PM (1995) Changes in soil phosphorus fractions and ecosystem dynamics across a long chronosequence in Hawaii. *Ecology* 76:1407–1424
- Cross AF, Schlesinger WH (1995) A literature-review and evaluation of the Hedley Fractionation—applications to the biogeochemical cycle of soil-phosphorus in natural ecosystems. *Geoderma* 64:197–214
- Dieter D, Elsenbeer H, Turner BL (2010) Phosphorus fractionation in lowland tropical rainforest soils in central Panama. *Catena* 82:118–125
- Dürr HH, Maybeck M, Dürr SH (2005) Lithologic composition of the Earth's continental surfaces derived from a new digital map emphasizing riverine material transfer. *Global Biogeochem Cy* 19 (GB4S10). doi:10.1029/2005GB002515
- Elser JJ, Bracken MES, Cleland EE, Gruner DS, Harpole WS, Hillebrand H, Ngai JT, Seabloom EW, Shurin JB, Smith JE (2007) Global analysis of nitrogen and phosphorus limitation of primary producers in freshwater, marine, and terrestrial ecosystems. 1135–1142
- Gleason SM, Read J, Ares A, Metcalfe DJ (2009) Phosphorus economics of tropical rainforest species and stands across soil contrasts in Queensland, Australia: understanding the effects of soil specialization and trait plasticity. *Funct Ecol* 23:1157–1166
- Harrison AF (1987) Soil organic phosphorus: a review of world literature. Wallingford, UK
- Hedley MJ, Stewart JWB, Chauhan BS (1982) Changes in inorganic and organic soil phosphorus fractions by cultivation practice and by laboratory incubations. *Soil Science Society of America journal* 46:970–976
- Hooper DU, Vitousek PM (1998) Effects of plant composition and diversity on nutrient cycling in serpentine grassland. *Ecological Monographs* 68:121–149
- Huenneke LF, Hamburg SP, Koide R, Mooney HA, Vitousek PM (1990) Effects of soil resources on plant invasion and community structure in Californian serpentine grassland. *Ecology* 71:478–491
- Jenny H (1941) Factors of soil formation: a system of quantitative pedology. McGraw Hill, New York
- Jenny H, Arkley RJ, Schultz AM (1969) The pygmy forest-podsol ecosystem and its dune associates on the Mendocino Coast. *Madroño* 20:60–74
- Jobbágy EG, Jackson RB (2001) The distribution of soil nutrients with depth: global patterns and the imprint of plants. *Biogeochemistry* 53:51–77
- Johnson AH, Frizano J, Vann DR (2003) Biogeochemical implications of labile phosphorus in forest soils determined by the Hedley fractionation procedure. *Oecologia* 135:487–499
- Kitayama K, Majalap-Lee N, Alba S (2000) Soil phosphorus fractionation and phosphorus-use efficiencies of tropical rainforests along altitudinal gradients of Mount Kinabalu, Borneo. *Oecologia* 123:342–349
- Kurtz AC, Derry LA, Chadwick OA (2001) Accretion of Asian dust to Hawaiian soils: isotopic, elemental and mineral mass balances. *Geochim Cosmochim Acta* 65:1971–1983
- Lajtha K, Schlesinger WH (1988) The biogeochemistry of phosphorus cycling and phosphorus availability along a desert soil chronosequence. *Ecology* 69:24–39

- Le Bayon R, Weiskopf L, Martinoia E, Jansa J, Frossard E, Keller F, Föllmi K, Gobat JM (2006) Soil phosphorus uptake by continuously cropped *Lupinus albus*: a new microcosm design. *Plant Soil* 283:309–321
- Lohse KA, Dietrich WE (2005) Contrasting effects of soil development on hydrological properties and flow paths. *Water Resour Res* 41:60
- Mage S, Porder S (in press) Parent material and topography determine soil phosphorus status in the Luquillo Mountains of Puerto Rico. *Ecosystems*
- Martinelli LA, Piccolo MC, Townsend AR, Vitousek PM, Cuevas E, McDowell W, Robertson GP, Santos OC, Treseder K (1999) Nitrogen stable isotopic composition of leaves and soil: tropical versus temperate forests. *Biogeochemistry* 46:45–65
- McDowell RW, Cade-Menun B, Stewart I (2007) Organic phosphorus speciation and pedogenesis: analysis by solution ^{31}P nuclear magnetic resonance spectroscopy. *Eur J Soil Sci* 58:1348–1357
- Miller AJ, Schuur EAG, Chadwick OA (2001) Redox control of phosphorus pools in Hawaiian montane forest soils. *Geoderma* 102:219–237
- Okin GS, Mahowald NM, Chadwick OA, Artaxo P (2004) Impact of desert dust on the biogeochemistry of phosphorus in terrestrial ecosystems. *Global Biogeochem Cy* 18:GB2005 2001–2009
- Olsen SR, Cole CV, Wantanabe FS (1954) Estimation of available phosphorus in soils by extraction with sodium bicarbonate, Washington, D.C.
- Oon TT (1971) Studies on a chronosequence near Reefton. University of Canterbury, Lincoln
- Peretyazhko T, Sposito G (2005) Iron(III) reduction and phosphorus solubilization in humid tropical forest soils. *Geochim Cosmochim Acta* 69:3643–3652
- Pett-Ridge J (2009) Contributions of dust to phosphorus cycling in tropical forests of the Luquillo Mountains, Puerto Rico. *Biogeochemistry* 94:63–80
- Porder S, Chadwick OA (2009) Climate and soil-age constraints on nutrient uplift and retention by plants. *Ecology* 90:623–636
- Porder S, Hilley GE (2011) Linking chronosequences with the rest of the world: predicting soil phosphorus content in denuding landscapes. *Biogeochemistry* 102:153–166
- Porder S, Paytan A, Vitousek PM (2005) Erosion and landscape development affect plant nutrient status in the Hawaiian Islands. *Oecologia* 142:440–449
- Porder S, Hilley GE, Chadwick OA (2007a) Chemical weathering, mass loss, and dust inputs across a climate by time matrix in the Hawaiian Islands. *Earth Planet Sci Lett* 258:414–427
- Porder S, Vitousek PM, Chadwick OA, Chamberlain CP, Hilley GE (2007b) Uplift, erosion, and phosphorus limitation in terrestrial ecosystems. *Ecosystems* 10:158–170
- Proctor J (2003) Vegetation and soil and plant chemistry on ultramafic rocks in the tropical Far East. *Perspect Plant Ecol Evol Systemat* 6:105–124
- Reich PB, Oleksyn J (2004) Global patterns of plant leaf N and P in relation to temperature and latitude. *Proc Natl Acad Sci* 101(30):11001–11006
- Richter D, Allen H, Li J, Markewitz D, Raikes J (2006) Bioavailability of slowly cycling soil phosphorus: major restructuring of soil P fractions over four decades in an aggrading forest. *Oecologia* 150:259–271
- Sanchez PA (1976) Properties and management of soils in the tropics. Wiley, New York
- Selmants PC, Hart SC (2010) Phosphorus and soil development: does the Walker and Syers model apply to semiarid ecosystems. *Ecology* 91:474–484
- Soderberg K, Compton JS (2007) Dust as a nutrient source for fynbos ecosystems, South Africa. *Ecosystems* 10:550–561
- Sokal RR, Rohlf FJ (2011) Biometry. 4 edition. W.H. Freeman
- Spear FS (1993) Metamorphic phase equilibria and pressure-temperature-time paths. Mineralogical Society of America, Washington
- Stevens PR (1968) A chronosequence of soils near the Franz Joseph Glacier. University of Canterbury, Canterbury
- Suchet PA, Probst J, Ludwig W (2003) Worldwide distribution of continental rock lithology: implications for the atmospheric/soil CO_2 uptake by continental weathering and alkalinity river transport to the oceans. *Global Biogeochem Cy* 17(2):1038. doi:10.1029/2002GB001891
- Syers JK, Johnston AE, Curtin D (2008) Efficiency of soil and fertilizer phosphorus use: reconciling changing concepts of soil phosphorus behavior with agronomic information. FAO, Rome
- Takyu M, Aiba S, Kitayama K (2002) Effects of topography on tropical lower montane forests under different geological conditions on Mount Kinabalu, Borneo. *Plant Ecology* 159:35–49
- Taylor SR, McClennan SM (1985) The continental crust: its composition and evolution. Blackwell Scientific, Oxford
- Tiessen H, Moir JO (1993) Characterization of available P by sequential extraction. In: Carter MR (ed) Soil sampling and methods of analysis. Lewis, Boca Raton, pp 75–86
- Turner BL (2008) Resource partitioning for soil phosphorus: a hypothesis. *J Ecol* 96:698–702
- Turner BL, Engelbrecht BMJ (2011) Soil organic phosphorus in lowland tropical rain forests. *Biogeochemistry* 103:297–315
- Turner BL, Condron LM, Richardson SJ, Peltzer DA, Allison VJ (2007) Soil organic phosphorus transformations during pedogenesis. *Ecosystems* 10:1166–1181
- Vitousek PM (1982) Nutrient cycling and nutrient use efficiency. *Am Nat* 119:553–572
- Vitousek PM (1984) Litterfall, nutrient cycling and nutrient limitation in tropical forests. *Ecology* 65(1):285–298
- Vitousek PM (2004) Nutrient cycling and limitation: Hawai'i as a model system. Princeton University Press, Princeton
- Vitousek PM, Howarth RW (1991) Nitrogen limitation on land and in the sea: How can it occur? *Biogeochemistry* 13:87–115
- Vitousek PM, Porder S, Houlton BZ, Chadwick OA (2010) Terrestrial phosphorus limitation: mechanisms, implications, and nitrogen-phosphorus interactions. *Ecol Appl* 20:5–15
- Walker TW, Syers JK (1976) The fate of phosphorus during pedogenesis. *Geoderma* 15:19