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**Phosphorus and iron cycling in deep saprolite,
Luquillo Mountains, Puerto Rico**

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17 **Abstract**

18 Rapid weathering and erosion rates in mountainous tropical watersheds lead to highly
19 variable soil and saprolite thicknesses which in turn impact nutrient fluxes and biological
20 populations. In the Luquillo Mountains of Puerto Rico, a 5 meter-thick saprolite contains high
21 microorganism densities at the surface and at depth overlying bedrock. We test the hypotheses
22 that the organisms at depth are limited by the availability of two nutrients, P and Fe. Many
23 tropical soils are P limited, rather than N limited, and dissolution of apatite is the dominant
24 source of P. We document patterns of apatite weathering and of bioavailable Fe derived from the
25 weathering of primary minerals hornblende and biotite in cores augered to 7.5 m on a ridgetop as
26 compared to spheroidally weathering bedrock sampled in a nearby roadcut.

27 Iron isotopic compositions of 0.5 N HCl extracts of soil and saprolite range from about
28 $\delta^{56}\text{Fe} = 0$ to -0.1 ‰ throughout the saprolite except at the surface and at 5 m depth where $\delta^{56}\text{Fe} =$
29 -0.26 to -0.64 ‰. The enrichment of light isotopes in HCl-extractable Fe in the soil and at the
30 saprolite-bedrock interface is consistent with active Fe cycling and consistent with the locations
31 of high cell densities and Fe(II)-oxidizing bacteria, identified previously. To evaluate the
32 potential P-limitation of Fe-cycling bacteria in the profile, solid-state concentrations of P were
33 measured as a function of depth in the soil, saprolite, and weathering bedrock. Weathering
34 apatite crystals were examined in thin sections and an apatite dissolution rate of 6.8×10^{-14} mol
35 $\text{m}^{-2} \text{s}^{-1}$ was calculated. While surface communities depend on recycled nutrients and atmospheric
36 inputs, deep communities survive primarily on nutrients released by the weathering bedrock and
37 thus are tightly coupled to processes related to saprolite formation including mineral weathering.

38 While low available P may limit microbial activity within the middle saprolite, fluxes of P from
39 apatite weathering should be sufficient to support robust growth of microorganisms in the deep
40 saprolite.

41
42 Keywords: phosphorus; iron isotopes; saprolite; apatite weathering rate; Fe(II)-oxidizing bacteria

43
44 **1. Introduction**

45 Except where recent landslides have occurred, thick saprolites in the Luquillo Mountains
46 isolate the weathering bedrock from the soil ecosystem. Despite high precipitation ($>4000 \text{ mm y}^{-1}$)
47 in the Rio Icacos watershed of the Luquillo Mountains, most water that reaches the soil moves
48 through the shallow soil layers and the water that does infiltrate to the deep saprolite on the
49 ridges does so slowly: $1.8 - 2.6 \text{ m y}^{-1}$ (Turner, 2001). Established tropical forests are typically
50 characterized by a closed nutrient cycle in which nutrients are tightly cycled within the surface
51 soil and biomass because the underlying substrates are highly weathered and thus nutrient poor
52 (e.g., Bruijnzeel, 1991). The majority of nutrients in precipitation and dry deposition in the Rio
53 Icacos watershed are thus likely rapidly scavenged by the abundant tropical vegetation and soil
54 organisms, leaving little to infiltrate to subsurface communities, as evidenced by very low DOC
55 concentrations in the deep saprolite porewaters (Murphy, 1995). Indeed, tracers such as Sr and Si
56 isotope ratios and Si/Ge ratios indicate that while vegetation and porewaters in the soil and
57 shallow saprolite of the Rio Icacos watershed contain atmospherically derived elements, middle
58 and deep saprolite porewaters (collected from nested suction water samplers) are dominated by
59 elements derived from bedrock weathering (Kurtz and Derry, 2004; Ziegler et al., 2005; Pett-

60 Ridge et al., 2009; Lugolobi et al., Subm.). Furthermore, the majority of the annual precipitation
61 falls as short, intense storm events during which runoff to the streams occurs through the shallow
62 saprolite only (Lugolobi et al., 2006). Deeper saprolite microbial communities are therefore
63 highly dependent upon weathering bedrock for nutrients (Buss et al., 2005). In the deep saprolite
64 of the Rio Icacos watershed, cell densities increase near the bedrock-saprolite interface where
65 Fe(II)-oxidizing bacteria were detected. Maximum growth rates were estimated for these
66 chemolithoautotrophic microorganisms and for their dependent heterotrophic communities based
67 on the rate of release of Fe(II) from silicate minerals during weathering at the bedrock-saprolite
68 interface (Buss et al., 2005). In Buss et al. (2005), cell densities (live + dead) in the saprolite
69 were estimated by direct counting and from DNA yields. The activity of the microorganisms was
70 not examined and it is possible that the organisms present at depth were merely dormant due to
71 P-limitation. In this paper, we compare P fluxes and P requirements to growth rates based on
72 Fe(II) fluxes to test whether the community at depth in these samples was nutrient (P)-limited or
73 energy (Fe(II))-limited. We also use Fe isotopes to examine the activity of Fe-cycling
74 microorganisms in the saprolite profile.

75 Phosphorus is an essential macronutrient, vital to all biological systems. Adenosine
76 triphosphate (ATP), one of the most important and abundant biomolecules in nature, is formed
77 during photosynthesis and cellular respiration and functions as an energy shuttle, providing
78 chemical energy for biosynthesis, cell motility, and osmotic transport of molecules through cell
79 membranes (Garrett and Grisham, 1999). Phosphorus is found in DNA and RNA as phosphate
80 ester bridges that link individual nucleotides, in cell membranes as phospholipids, and as a
81 component of many signaling molecules, enzymes, and coenzymes (Frausto da Silva and
82 Williams, 191; Garrett and Grisham, 1999). However, P availability is commonly very low in

83 tropical soils, a fact that is often attributed to the strong sorption of P to Fe and Al oxides (e.g.,
84 Sanchez, 1976; Vitousek, 1984; Olander and Vitousek, 2005). In contrast, tropical soils are
85 typically not N limited (e.g., Vitousek and Sanford, 1986). In the tropical Luquillo Mountains of
86 northeastern Puerto Rico, low rates of NO_3^- leaching and export (McDowell and Asbury, 1994)
87 result primarily from effective N retention via dissimilatory nitrate reduction to ammonium
88 (Templer et al., 2008). High rates of NH_4^+ production via rapid decomposition of soil organic
89 matter also contribute to N availability and retention in tropical soils (Vitousek and Sanford,
90 1986). In saprolite porewaters in the Rio Icacos watershed, N concentrations increase with depth
91 on both ridgetops and slopes (White et al., 1998) suggesting that, like soils, deep saprolite is also
92 not N limited. It is interesting to note that of the two elements that are most often limiting in
93 terrestrial systems, N and P, only P comes directly from rocks (Wardle et al., 2004).

94 Pools of P in a forest soil may include primary minerals (predominantly apatite),
95 secondary minerals (associated with Fe or Al oxides or clays), aqueous species in pore waters
96 (inorganic or organic complexes), and solid organic P (contained in biomass and other organic
97 matter). External sources of P to a soil system include bedrock weathering and atmospheric
98 deposition (precipitation and dust). Most of the P associated with secondary minerals, biomass,
99 and organic matter represent internal sources of P that are recycled and transferred between pools
100 on various timescales during the lifetime of an ecosystem. In most soil profiles, P is supplied into
101 the system almost entirely by weathering due to low atmospheric input of P (Walker and Syers,
102 1976). However, Caribbean island soils receive significant nutrient inputs from African dust and
103 volcanic ash (Graham and Duce, 1982; Heartsill-Scalley et al., 2007; Muhs et al., 2007). Thick,
104 highly weathered saprolites on the ridges of the Luquillo Mountains of Puerto Rico effectively
105 isolate surface soils from weathering bedrock (e.g., Buss et al., 2005), thus atmospheric

106 deposition may dominate exogenous input of P to the ridgetop soils (Pett-Ridge, 2009). In
107 contrast, mineral weathering is expected to dominate P input to deep saprolite or where saprolite
108 is thin due to topography or erosion. Landslides, which are the dominant mechanism of erosion
109 in the Luquillo Mountains (Simon et al., 1990), increase access to mineral-derived nutrients,
110 notably apatite, which affects the rate of vegetation re-growth on landslide scars (e.g., Zarin and
111 Johnson, 1995; Frizano et al., 2002).

112 Stable Fe isotopes provide a promising new tool for tracing biogeochemical Fe cycles in
113 soils and weathering systems. Iron isotope systematics have been studied for multiple processes
114 that are relevant to soil systems including i) inorganic dissolution (mobilization of Fe from
115 minerals by H⁺), ii) organic dissolution (mobilization of Fe by organic ligands or
116 microorganisms), iii) reductive dissolution (reduction of mineral-bound Fe(III) followed by
117 mobilization of Fe(II)), iv) precipitation of Fe(III)-(hydr)oxides from solution, v) adsorption of
118 Fe onto oxide or clay minerals, and vi) uptake of Fe by plants or microorganisms. Fractionations
119 favoring the release of the light isotope (⁵⁴Fe) to solution leaving an isotopically heavy solid
120 (enriched in ⁵⁶Fe) have been documented for organic dissolution of hornblende by bacteria,
121 organic acids, and siderophores (Brantley et al., 2001b; 2004) and for ligand-controlled Fe
122 relocation in soils (Wiederhold et al., 2007b). Organic dissolution of goethite did not produce an
123 isotopic fractionation (Brantley et al., 2004), nor did inorganic dissolution of hornblende or
124 goethite (Brantley et al., 2001b; 2004). Reductive dissolution of goethite, hematite, and
125 ferrihydrite in the presence of bacteria generates a solution that is isotopically light with respect
126 to the starting mineral (e.g., Beard et al., 1999; 2003; Icopini et al., 2004; Crosby et al., 2005;
127 2007), which leads to a loss of isotopically light Fe from soils (Thompson et al., 2007;
128 Wiederhold et al., 2007b). However, fractionation may occur via isotopic exchange between

129 aqueous Fe(II) and sorbed Fe(II) , rather than during reductive dissolution, because adsorption of
130 Fe(II) onto goethite preferentially removes ^{56}Fe from solution, with or without bacteria (Brantley
131 et al., 2004; Icopini et al., 2004). Similarly, precipitation of ferrihydrite also concentrates the
132 heavier isotope in a solid product while the solution becomes isotopically lighter (Bullen et al.,
133 2001; Teutsch et al., 2005). Plants that obtain Fe by acidifying the rhizosphere to promote
134 reductive dissolution of Fe(III)-oxides preferentially take up Fe that is isotopically light relative
135 to the surrounding soil (Guelke and Von Blanckenburg, 2007). In contrast, uptake of Fe(III)-
136 siderophore complexes does not result in a fractionation of Fe in grasses that produce
137 phytosiderophores (Guelke and Von Blanckenburg, 2007).

138 Here we use Fe isotope ratios to investigate controls on the bioavailable fraction of Fe.
139 Iron isotopes are measured in the fraction of Fe liberated from soil and saprolite samples by a
140 dilute HCl leach, which is often associated with the most reactive, or bioavailable, fraction of Fe
141 in soils and sediments (e.g., Fantle and DePaolo, 2004; Buss et al., 2005; Severmann et al., 2006;
142 Wiederhold et al., 2007b). In addition to colloid-bound Fe, organic-bound Fe, and the (typically
143 minute) aqueous Fe(II), it is this “reactive Fe” that is transported from weathering profiles to
144 rivers and oceans and dominates the Fe isotope signatures of these bodies of water (Fantle and
145 DePaolo, 2004). In high silicate soils, Fe within this reactive pool is expected to be isotopically
146 light relative to bedrock and residual material (Fantle and DePaolo, 2004; Wiederhold et al.,
147 2007b), which may indicate active biogeochemical cycling of Fe. For example, complexation of
148 Fe by organic ligands or reductive dissolution of Fe(III)-(hydr)oxides would cause an excursion
149 towards a lighter Fe isotope signature within the reactive Fe pool, while Fe uptake by vegetation
150 would likely yield a heavier Fe isotope signature (Fantle and DePaolo, 2004; Wiederhold et al.,
151 2006; Wiederhold et al., 2007a, b). In soils or regolith where the residual (non-HCl extractable)

152 Fe is dominated by Fe(III)-hydroxides, isotopic distinction between the two pools may be less
153 than in silicate soils due to rapid isotopic exchange between sorbed Fe(II) and Fe(III)-hydroxides
154 (Pedersen et al., 2005). Here we test the hypothesis that HCl-extractable Fe will be isotopically
155 light in the biologically active zones of the Rio Icacos weathering profile, relative to zones in
156 which biological activity is suppressed due to limited nutrient and energy fluxes.

157

158 **2. Methods**

159 **2.1. Field Site and Sample Collection**

160 The Rio Icacos watershed in the Luquillo Experimental Forest of northeastern Puerto
161 Rico is predominantly located in a lower montane wet colorado forest that receives over 4000
162 mm of rain annually. The watershed is underlain by the Rio Blanco quartz diorite bedrock, which
163 weathers spheroidally resulting in rounded corestones of about 2 m in diameter, surrounded by
164 0.2 – 2 m thick zones of concentric, partially weathered rock layers called rindlets (Turner et al.,
165 2003; Buss et al., 2004; Buss et al., 2005; Fletcher et al., 2006; Buss et al., 2008). The rindlet
166 zones are mantled by 200 ka regolith, dated using ^{10}Be (Brown et al., 1995), and is comprised of
167 2-8 m of saprolite and 0.5-1 m of highly weathered Picacho-Ciales complex soils, previously
168 classified as Ultisols (Boccheciamp et al., 1977), but now considered Inceptisols due to weak B
169 horizon development (USDA NCRS, 2002).

170 Two 5.7 cm diameter cores of soil and saprolite were collected 1 m apart by hand
171 augering to 7.5 m and 5.0 m depth at the top of the Guaba Ridge in the Rio Icacos watershed
172 (latitude 18°16.903'N, longitude 65°47.418'W), which has been mapped by others (Murphy et
173 al., 1998; White et al., 1998; Turner et al., 2003; Buss et al., 2008). Samples were taken from the
174 auger at 0.15 – 0.3 m depth intervals. The deeper core penetrated the rindlet zone below 5 m

175 depth. The sampling procedure was described by Buss et al. (2005). Redoximorphic features
176 such as gleying or mottling were not observed in the saprolite samples, but several zones of pink
177 and black Mn-oxide concentrations were identified (Buss et al., 2005). The saprolite is formed
178 on a cuchillo, or knife-edge ridge, and is not significantly influenced by lateral flow of
179 groundwater at depth (White et al., 1998; Lugolobi et al., 2006). The pH of the soil and saprolite
180 porewater is 4.0 – 5.4 (White et al., 1998). The edge of a corestone and the complete 49 cm
181 section of rindlets above the corestone were sampled at a nearby roadcut exposed on Route 191
182 (latitude 18°16.216'N, longitude 65°47.055'W), preserving the position and orientation of the
183 individual rindlets as described by Buss et al. (2008). The corestone was located beneath about 2
184 m of saprolite forming a small local topographic high.

185

186 **2.2. Phosphorus and Apatite Analyses**

187 Phosphorus was measured by inductively coupled plasma atomic emission spectrometry
188 (ICP-AES) after lithium metaborate fusion digestion (SGS Mineral Laboratories, Ontario,
189 Canada) of pulverized and sieved (150 µm) corestone, rindlet, and saprolite samples. Apatite
190 crystals were identified in thin sections of the corestone and rindlets using backscattered electron
191 (BSE) imaging and energy dispersive X-ray spectrometry (EDS) on an FEI Quanta 400 SEM.
192 Point counting of apatite crystals was performed on backscattered images using XT-Docu
193 software (v. 3.2, Soft-Imaging System GmbH, Münster, Germany), which calculates the volume
194 of each user-defined phase based on the backscatter grayscale value. This technique has been
195 used to measure porosity and to point count mineral phases in weathering rocks (Dorn, 1995;
196 Dixon et al., 2006; Buss et al., 2008).

197

198 **2.3. Fe Isotope Analysis**

199 Iron in soils and sediments exist in many different forms (e.g., as readily exchangeable
200 ions; precipitated as, or bound to, oxide or hydroxide phases; bound to organic matter; in
201 carbonates; or in silicates). These fractions are often extracted sequentially by stronger and
202 stronger leaching procedures. Extractions are favored over total digests because only average
203 isotope ratios of all different Fe phases are obtained from total digests. Extraction of soils and
204 sediments with dilute HCl is expected to liberate readily exchangeable ions, adsorbed Fe, some
205 organic-bound Fe, and poorly crystalline Fe oxides and hydroxides (Wiederhold et al., 2007b)
206 and represent a more reactive, or bioavailable, Fe pool than the bulk solid (Emerson, 2002). Iron
207 isotopes were measured in 0.5 N HCl extracts performed on soil and saprolite samples augered
208 from the Guaba Ridge. Iron isotopes are not fractionated by this extraction procedure:
209 fractionation did not occur during dissolution of goethite or hematite in 0.5 N HCl, even when
210 dissolution was incomplete (Skulan et al., 2002; Wiederhold et al., 2006). Soil and saprolite
211 samples were air dried and gently ground only to break up aggregates before sieving to 2 mm.
212 Samples (0.5 g) were then combined with 10 ml 0.5 N HCl in 15 mL centrifuge tubes and
213 agitated on an end-over-end shaker at room temperature for 17 hours, followed by centrifugation
214 at 4000 x g for 10 minutes (Buss et al., 2005). Supernatants were decanted, centrifuged again,
215 and filtered to 0.4 μm (SFCA-membrane syringe filter, Cole-Parmer). Concentrations of ferrous
216 iron in the extracts were measured by ultraviolet-visible (UV/Vis) spectrophotometry as
217 described and reported by Buss et al. (2005). Total Fe was measured by inductively coupled

218 plasma mass spectrometry (ICP-MS) and ferric iron was calculated as the difference between
219 total and ferrous iron concentrations, as detailed in Buss et al. (2005).

220 Iron was separated from other cations in the HCl extracts following a standard ion
221 exchange column method using AG MP-1 (100-200 mesh) resin (BIORAD) as described by
222 Brantley et al. (2004). Post-purification iron yield was measured volumetrically and found to be
223 better than 95%. Fe isotopes were measured at Washington State University using a multi-
224 collector inductively coupled plasma mass spectrometer (MC-ICP-MS, Neptune®,
225 ThermoFinnigan). The Fe concentration in each sample was adjusted to 3 ppm and a 3 ppm Cu
226 standard was added to each. Sample measurements were bracketed with the standard-sample-
227 standard technique. The mass bias in each sample was corrected using the exponential law
228 (Arnold et al., 2004) and by using the graphical techniques developed by Maréchal et al. (1999).
229 Both methods of data reduction resulted in values that were within the reported 2σ error (± 0.1
230 ‰). This error was calculated by using multiple measurements of the Fe isotope ratio of goethite
231 throughout four weeks of analysis (sample measured 25 times). The $\delta^{56}\text{Fe}$ (‰) values were
232 calculated relative to the international Fe standard IRMM-014, using the following equation:

233

$$234 \quad \delta^{56/54}\text{Fe} = \left(\frac{(^{56}\text{Fe}/^{54}\text{Fe})_{\text{sample}}}{(^{56}\text{Fe}/^{54}\text{Fe})_{\text{IRMM}}} - 1 \right) \times 1000 \quad (1).$$

235 3. Results

236 To evaluate mass transfer (loss or gain of an element relative to the parent rock
237 composition) of P in the Rio Icaos weathering profile, we calculate Ti-normalized solid-state

238 concentrations of P, C_w , which may differ from the measured value, C , due to changes in density
239 and concentrations of other elements during weathering:

240

$$C_w = C \left(\frac{C_{Ti,p}}{C_{Ti,w}} \right) \quad (2)$$

241 where $C_{Ti,p}$ (mol kg⁻¹) is the solid-state concentration of Ti in the protolith and $C_{Ti,w}$ is the solid-
242 state concentration of Ti in the weathered material (Ti measured by ICP-AES). Open-system
243 mass transport (e.g., Brimhall and Dietrich, 1987; Anderson et al., 2002) is quantifiable in the
244 Rio Icacos weathering profiles because the protolith is homogenous, of uniform age, and
245 contains a relatively inert component that persists in the weathered material (Chadwick et al.,
246 1990). White et al. (1998) and Buss et al. (2008) identified Ti as relatively immobile in the Rio
247 Icacos saprolite relative to the bedrock based on calculations of very low volumetric strain with
248 respect to Ti. Volumetric strain (here the change in volume due to expansion or collapse), should
249 be near-zero in isovolumetrically weathered material such as saprolite.

250 The average of five analyses from a single corestone adjacent to the rindlets sampled was
251 used as the protolith composition for C_w calculations of rindlet samples (Buss et al., 2008). The
252 deepest sample (7.24 m) obtained from the augered cores on the Guaba Ridge was used as the
253 protolith for calculations performed on the core samples. Ti concentrations in the bedrock vary
254 slightly throughout the watershed (Turner et al., 2003) and thus it is appropriate to use the least
255 weathered sample obtainable under a given weathering profile as the parent material. Normalized
256 P concentrations (C_w) increase with increasing depth into the regolith, with a dramatic increase at
257 the bottom of the saprolite at 5 m (Figure 1). An increase in P at approximately 2.5 m depth
258 corresponds to a visible, biological, and chemical heterogeneity in the saprolite interpreted to be

259 a rindlet that has not fully saprolitized: a ‘ghost rindlet’ (Buss et al., 2005). Below 5 m depth
260 (where the auger penetrated the rindlet zone), normalized P concentrations range from 0.01 –
261 0.02 mol kg⁻¹, which is consistent with P concentrations in the rindlet zone sampled in the
262 roadcut (Figure 2). The gradients in C_w over the augered rindlet zone and the roadcut rindlet zone
263 are equivalent when the rindlet zone thicknesses are scaled so that the two interfaces that
264 delineate the rindlet zone (the saprolite-rindlet and rindlet-bedrock interfaces) coincide for both
265 sample sets (Figure 2).

266 Dissolution of apatite within the rindlet zone is apparent in thin section as well as in the P
267 elemental concentration profiles of the bulk materials. Loss of apatite occurs with increasing
268 distance from the corestone-rindlet interface (Table 1). Apatite grains in the bedrock exist along
269 grain boundaries of other minerals or as inclusions, mostly within hornblende, but also
270 occasionally within plagioclase or primary Fe oxides. Apatite inclusions are seen to dissolve out
271 of relatively intact crystals such as hornblende or plagioclase (Figure 3). Phosphorus-containing
272 secondary minerals were not detected.

273 Fe isotopic compositions in the HCl extracts, $\delta^{56}\text{Fe}$, of the soil and saprolite range from
274 about 0 to -0.1 ± 0.1 ‰ throughout most of the profile, consistent with values for igneous rocks
275 (Beard et al., 2003). Only at the surface (above ~ 1.2 m depth) and in the deepest saprolite (at 4.9
276 m depth) did we observe distinct variation in isotopic compositions: values were observed to be
277 as light as -0.64 and -0.40‰ in those zones respectively (Table 2, Figure 4). These zones of
278 lighter Fe isotope ratios correspond to zones of higher concentrations of extractable Fe, cell
279 numbers, DNA yields, and Fe(II)-oxidizing bacteria (Buss et al, 2005; Figure 4).

280

281 **4. Discussion**

282 **4.1. Phosphorus Flux and Apatite Weathering**

283 Changes in P concentration with depth in regolith generally represent depletion profiles,
284 biogenic profiles, or depletion-addition profiles, (or a combination) (Brantley et al., 2007;
285 Brantley et al., 2008). A depletion profile occurs when P-bearing minerals dissolve and P is
286 leached from the system and a biogenic profile is created when P that is solubilized at depth is
287 transported upward and stored in the upper soil by biological processes. A depletion-addition
288 profile is characterized by mobilization from the upper soil layer and enrichment in lower layers.
289 A fourth type of profile is also possible: an addition profile, if atmospheric deposition or addition
290 of P-rich fertilizers introduces P into the system. The slope of a concentration profile provides
291 information about the rates and mechanisms of the depletion, addition, or biological processes
292 that control the transfer of mass (e.g., White, 2002; Brantley et al., 2008; Buss et al., 2008). In
293 the Rio Icacos watershed, the thicknesses of the weathering profiles are maintained by a positive
294 feedback between weathering and erosion, controlled by the infiltration of aqueous O₂ to the
295 weathering interface (Fletcher et al., 2006). Although the regolith and rindlet zones of the
296 roadcut and augered site differ in thickness, that the concentration profiles of P in these two
297 locations are consistent (that the same amount of P is lost from interface-to-interface, Figure 2)
298 points to the same mechanism of P mass transfer in both profiles.

299 Phosphorus in soils exists in a variety of forms, many of which are considered to be
300 occluded or only sparingly soluble and thus not readily available to biota. However, these
301 recalcitrant and occluded pools of P (sorbed to Al and Fe oxides, trapped within soil aggregates,
302 or contained within clays or phosphate minerals) are slowly liberated and thus can be considered

303 bioavailable when integrating over longer (e.g., decadal) timescales (Cumming and Weinstein,
304 1990; Richter et al., 2006). In addition, P sequestered in Fe(III)-(hydr)oxides can be liberated on
305 much shorter timescales by reductive dissolution in environments subjected to redox
306 fluctuations. In surface soils in the nearby Bisley Research Watersheds, also in the Luquillo
307 Forest, periodic O₂ depletion (in approximately 2 week intervals) related to high biological
308 activity, warm temperatures, and abundant rainfall, causes redox fluctuations that lead to
309 repeated cycles of reductive dissolution and oxidative re-precipitation of Fe(III)-(hydr)oxides
310 (Liptzin and Silver, 2009). The P released during the reductive half-cycle is immediately taken
311 up by the biota, bypassing the “labile” P pool (NaHCO₃-extractable) (Liptzin and Silver, 2009).
312 Although the deep saprolite is not subjected to the environmental fluctuations of the surface
313 soils, microscale redox-cycling at depth remains likely. Indeed, visible Mn-oxide gradients in the
314 saprolite that are coincident with zones of high cell densities indicate local zones of redox-
315 cycling associated with microbial growth (Buss et al., 2005).

316 In deep saprolite profiles such as on the Guaba Ridge, where atmospheric and recycled
317 (e.g., leaf litter) P are not available, apatite dissolution during bedrock weathering provides a
318 source of P for the deep microbial communities. These communities are directly dependent on
319 the flux of P from the weathering of apatite crystals in the rindlet zone. Laboratory experiments
320 have demonstrated the ability microorganisms to enhance dissolution of apatite to obtain P (e.g.,
321 Welch et al., 2002; Schaperdoth et al., 2007) indicating that apatite-bound P can be considered a
322 bioavailable form. In the Rio Icacos watershed, apatite weathers in the rindlet zone, often within
323 rock layers where porosity is insufficient to host microorganisms (Figure 3), thus microbial
324 dissolution of apatite is not considered a dominant process relative to abiotic dissolution. Much
325 of the P that is released by apatite dissolution is lost, as evidenced by the decline in P

326 concentrations with decreasing depth (Figures 1 and 2). Remaining P is either taken up by
327 microorganisms or mineralized, most likely sorbed to Fe(III)-(hydr)oxides. Phosphorus-
328 containing secondary minerals were not detected in the rindlet zone.

329 When the concentration of a mobile element (e.g., P) in a soil reflects dissolution without
330 concomitant secondary mineral precipitation, it demonstrates a decrease in the solid-state
331 concentration C_0 at depth z_l to C_w at a shallower depth z_0 (White, 2002) and can be characterized
332 as a depletion profile (Brantley et al., 2008). The slope of such a concentration–depth plot can be
333 related to the weathering velocity, ω , or rate of advance of weathering into unaltered (parent)
334 material, and the weathering rate, R , of the mineral supplying the mobile element. Here C_0
335 corresponds to the solid-state concentration of the element within the parent rock and C_w is the
336 solid-state concentration of the element in the weathered material at depth z . While such
337 depletion profiles often show curvature (Brantley et al., 2008), they can often be fitted
338 satisfactorily using linear regression to calculate a slope. The reaction rate R ($\text{mol m}^{-2} \text{s}^{-1}$) for a
339 given mineral in a weathering profile is calculated from the elemental distribution in the profile
340 using the following expression from White (2002):

$$R = 10^{-3} \frac{1}{\varphi \nu s} \frac{\omega}{b_s} \quad (3)$$

341 where φ is the mass fraction of the mineral in the weathering material (g g^{-1}), ν is the
342 stoichiometric coefficient of the element in the mineral (mol mol^{-1}), s is the specific surface area
343 of the mineral ($\text{m}^2 \text{g}^{-1}$), b_s is the weathering gradient (m kg mol^{-1}), and ω is the weathering
344 velocity (m s^{-1}), which is also known as the weathering advance rate or the regolith propagation
345 rate. The weathering velocity is calculated as the thickness of the profile, Δz , divided by the time
346 required to form the profile, t :

$$\omega = \frac{\Delta z}{t} \quad (4)$$

347 The methodology of White (2002) permits the calculation of solid-state reaction rates R
 348 for minerals in a weathering profile from the elemental distribution in the profile. Here we use
 349 Equation 3 (White, 2002) to quantify a weathering rate for apatite across the rindlet zone in the
 350 Rio Icacos watershed as a function of the average weathering velocity, $\omega = 43 \text{ m Ma}^{-1}$ (Brown et
 351 al., 1995). We consider the gradient in P across the rindlet zone ($b_s = 36.3 \text{ m kg mol}^{-1}$, Figure 2)
 352 and mineralogical parameters $\varphi = 0.008 \text{ g g}^{-1}$ for apatite (determined by digital point counting
 353 and converted to mass units), and $v = 3 \text{ mol P mol}^{-1}$. We calculate a geometric surface area, $s =$
 354 $0.023 \text{ m}^2 \text{ g}^{-1}$, by using an average grain size of $80 \text{ }\mu\text{m}$ and a cubic volume (Brantley et al., 1999).
 355 The resulting rate of apatite weathering is $6.8 \times 10^{-14} \text{ mol m}^{-2} \text{ s}^{-1}$, or $\log R = -13.2$. This rate is
 356 several orders of magnitude slower than apatite dissolution rates measured in the laboratory
 357 (Figure 5, Valsami-Jones et al., 1998; Welch et al., 2002; Guidry and Mackenzie, 2003,
 358 Schaperdoth et al., Unpub.), which is expected when comparing field rates to laboratory rates
 359 (White and Brantley, 2003). The only other field-based rate of apatite weathering that we are
 360 aware of is normalized to the volume of soil rather than the specific surface area of the mineral
 361 and thus cannot be directly compared (Nezat et al., 2004).

362 The apatite weathering profile and weathering velocity are directly related to the rate at
 363 which P is released from apatite. The flux of an element j , in terms of unit volume: F_j ($\text{mol } j \text{ m}^{-3}$
 364 s^{-1}), can describe the rate at which apatite-derived P is supplied to the deep saprolite microbial
 365 community:

$$F_j = 10^{-3} \frac{\omega \rho}{\varphi b_s} \quad (5)$$

367 where j is phosphorus and ρ is the density of the weathering material, which ranges from $1.83 \times$
368 10^6 to 2.7×10^6 g m^{-3} over the rindlet zone (Buss et al., 2008). Using this range of density values
369 yields: $F_p = 8.6 \times 10^{-9}$ to 1.3×10^{-8} $\text{mol P m}^{-3} \text{ s}^{-1}$.

370 Buss et al. (2005) estimated maximum rates of microbial growth in the deepest saprolite
371 at this site based on the flux of Fe(II) from the weathering bedrock, assuming Fe(II)-oxidizing
372 bacteria as the dominant primary producers. These organisms are chemolithoautotrophs, that is,
373 they use inorganic substrates for energy (e.g., Fe) and fix CO_2 to create organic carbon
374 (autotrophy). The calculated growth rates, β , were 6.9×10^{-8} $\text{mol biomass C m}^{-3} \text{ s}^{-1}$ for Fe(II)-
375 oxidizing bacteria and 3.5×10^{-8} $\text{mol C m}^{-3} \text{ s}^{-1}$ for heterotrophic bacteria. These latter bacteria are
376 dependent on the organic carbon produced by the Fe(II)-oxidizers because the dissolved organic
377 carbon (DOC) in porewaters at these depths is extremely low: $125 \mu\text{M}$ (Murphy, 1995) and
378 therefore the flux of DOC from the surface is insignificant relative to the flux of organic carbon
379 produced by autotrophy: $\sim 10^{-7}$ vs 10^{-4} $\text{mol C m}^{-3} \text{ h}^{-1}$, respectively (Buss et al., 2005).

380 To estimate the flux of P required, F_{req} ($\text{mol P m}^{-3} \text{ s}^{-1}$), to maintain a given growth rate, β
381 ($\text{mol C m}^{-3} \text{ s}^{-1}$), we divide the growth rate by the molar C:P ratio of the cells, X (mol mol^{-1}):

$$382 \quad F_{req} = \frac{\beta}{X} \quad (6).$$

383 The molar C:P ratio measured mixed cultures of P-limited lakewater heterotrophic
384 bacteria has been reported to lie in the range 80:1 to 100:1 (Jurgens and Gude, 1990). Other
385 values in the literature range from 57:1 to 100:1 for several individual species of P-limited, non-
386 marine, environmental bacteria (Jurgens and Gude, 1990). Taking a C:P ratio of 100 as a rough
387 estimate, we can use Equation 6 to estimate the flux of P required to support microbial growth at
388 the rates calculated by Buss et al. (2005): $F_{req} = 6.9 \times 10^{-10}$ and 3.5×10^{-10} $\text{mol P m}^{-3} \text{ s}^{-1}$ for the

389 Fe(II)-oxidizing and heterotrophic communities, respectively. These fluxes are less than the flux
390 of P provided by apatite weathering, F_P (Equation 5). Phosphorus requirements vary among
391 specific organisms and therefore we may be underestimating F_{req} , but because actual growth
392 rates are expected to be lower than the maximum rates estimated by Buss et al. (2005), these
393 results suggest that P is not limiting at the saprolite-bedrock interface.

394

395 **4.2. Fe Isotopic Composition of the Regolith Profile**

396 The HCl extraction is expected to liberate aqueous Fe; Fe contained within
397 microorganisms and biofilms; and weakly sorbed, amorphous, or poorly crystalline solid Fe
398 (Emerson, 2002; Buss et al., 2005; Wiederhold et al., 2007b). Thus we consider two general
399 reservoirs of Fe in the weathering profile: the extractable reservoir and the non-extractable
400 reservoir, which contains well-crystallized phases including Fe-silicates and goethite. Significant
401 sequestration of Fe in recalcitrant organic material is unlikely because concentrations of organic
402 C are extremely low below 1 m depth (Buss et al., 2005).

403 An enrichment of light Fe isotopes, such as we measured at the top and bottom of the Rio
404 Icaos weathering profile, is created by preferential input of ^{54}Fe to the extractable reservoir,
405 preferential removal of ^{56}Fe , or both. At the bottom of the saprolite, input to the reservoir of
406 HCl-extractable Fe is dominated by complete and rapid dissolution of hornblende, which occurs
407 only within a 7 cm zone at the rindlet-saprolite interface (Buss et al., 2008). Inorganic dissolution
408 of hornblende does not produce a fractionation in Fe isotopes in laboratory experiments;
409 however, dissolution of hornblende in the presence of organic acids, siderophores, or bacteria
410 preferentially releases ^{54}Fe via a kinetic isotope effect, producing a solution that is as much as

411 0.8‰ lighter than the mineral (Brantley et al., 2001a; Brantley et al., 2004). Organic dissolution
412 of hornblende is thus consistent with the enrichment in light Fe isotopes and the higher cell
413 densities at the bedrock-saprolite interface. Although the Rio Icacos weathering profile is
414 characterized by oxidation processes (White et al., 1998; Buss et al., 2005; Fletcher et al., 2006;
415 Buss et al., 2008) and neither Fe(III)-reducing bacteria nor redoximorphic features (e.g.,
416 mottling) have been detected in the saprolite (Buss et al., 2005), reductive dissolution cannot be
417 entirely ruled out. Microaerophilic, circumneutral Fe(II)-oxidizing bacteria were found in the
418 deep saprolite (Buss et al., 2005), which implies that oxygen may be depleted at depth, possibly
419 within microenvironments. Microscale redox cycling of Fe by bacteria has been demonstrated in
420 circumneutral sediments (Sobolev and Roden, 2002; Roden et al., 2004). Regardless, the rapid
421 dissolution of hornblende clearly dominates Fe input to the extractable reservoir at the bedrock-
422 saprolite interface.

423 Isotopically light extractable Fe also correlates with a larger reservoir of HCl-extractable
424 Fe and high cell densities in the top meter of the weathering profile, which comprises the soil and
425 rooting zone. Organic dissolution of biotite (and possibly Fe-bearing dust), decomposition of
426 isotopically light vegetation, and microbial or plant-mediated reductive dissolution of Fe(III)-
427 (hydr)oxides may all contribute to inputs of isotopically light Fe to the HCl-extractable reservoir
428 in the surface soil.

429 The higher concentration of Fe in the HCl-extracts at the top and bottom of the profile
430 relative to the middle saprolite indicates that input to the reservoir of extractable Fe is faster than
431 output from the reservoir in these zones. Organic dissolution of hornblende by organic ligands or
432 bacteria is substantially faster than inorganic dissolution (Kalinowski et al., 2000; Liermann et
433 al., 2000; Brantley et al., 2001b; Brantley et al., 2004; Buss et al., 2007), producing a “pulse” of

434 isotopically light Fe at the start of the hornblende weathering process. Calculations of C_w for Fe
435 in the saprolite and rindlets (Buss et al., 2005; 2008) are approximately constant with depth,
436 indicating that Fe is conserved within the system. Therefore, the only mechanism for removing
437 Fe from the extractable reservoir is by sequestration within well-crystallized Fe(III)-(hydr)oxides
438 either by re-crystallization of ferrihydrite to form goethite or hematite or possibly diffusion of
439 sorbed Fe into the crystalline phases. The rate of crystallization is a function of the concentration
440 of the ferrihydrite precursor, but can be affected by redox cycling and sorption processes.
441 Repeated redox cycling of Fe has been shown to increase the crystallinity of Fe(III)-(hydr)oxides
442 and decrease the size of the HCl-extractable Fe reservoir (Thompson et al., 2006). However, the
443 formation of goethite can be retarded by the sorption onto ferrihydrite of organic acids including
444 citrate and meso-tartrate, simple sugars including glucose and maltose, and silicate ions (Cornell,
445 1987). In contrast, adsorption of Fe(II) onto ferrihydrite substantially accelerates the formation of
446 goethite, likely because it can act as a reductant, encouraging dissolution of ferrihydrite (Yee et
447 al., 2006). A sorbed Fe(II) atom oxidizes and precipitates as goethite, while a ferrihydrite Fe(III)
448 atom is reduced and propagates the process. Because the heavier isotope preferentially partitions
449 into the oxidized product during equilibrium isotope exchange between Fe(II) and Fe(III), this
450 process could contribute to the isotopically light signature of the extractable reservoir (Icopini et
451 al., 2004), allowing it to persist for some time after the dissolving hornblende becomes depleted
452 in ^{54}Fe . Although batch experiments demonstrated rapid isotopic equilibration between poorly
453 crystalline and well-crystallized Fe(III)-hydroxides when exposed to Fe(II) (Pedersen et al.,
454 2005), such equilibration is expected to be significantly slower in the hydrologically unsaturated
455 (vadose zone) saprolite. Unlike surface soils, the deep saprolite is not chemically or
456 hydrologically affected by precipitation events or seasonal cycles and thus the chemical

457 composition, moisture content, O₂ partial pressure, and reaction rates are stable over relatively
458 long timescales in the deep saprolite (White et al., 1998), at least at the bulk sampling scale (i.e.,
459 there may be more variability within microenvironments). However, the potential for Fe isotopic
460 transience in the HCl-extractable reservoir due to aqueous Fe(II)-exchange with Fe(III)-
461 hydroxides or repeated redox cycling of Fe (Thompson et al., 2006) should be noted.

462 Biological activity at the bedrock-saprolite interface and in the surface soil may slow the
463 output of Fe from the extractable reservoir by organic complexation of Fe in solution or sorption
464 of microbial products such as organic acids or sugars onto ferrihydrite. However, once the input
465 of Fe from hornblende dissolution (which becomes isotopically heavier as dissolution
466 progresses) is exhausted, it is only a matter of time before the extractable Fe crystallizes into a
467 non-extractable form, homogenizing the two isotopic pools into a single reservoir. Without the
468 large flux of Fe from the dissolution of hornblende (Buss et al., 2008), active microbial
469 communities can no longer be supported and this is reflected in the low cell densities, extremely
470 low extractable Fe concentration, and near-zero $\delta^{56}\text{Fe}$ within the middle saprolite. In the
471 saprolite, Fe exists within oxide minerals and biotite, which weathers to kaolinite throughout the
472 saprolite (Murphy et al., 1998). The very low concentrations of HCl-extractable Fe in the middle
473 saprolite may also reflect a history of redox cycles at the rindlet-saprolite interface, which can
474 decrease the size of this pool (Thompson et al., 2006) (Figure 1b). It is also relevant to note that
475 redox cycling of Fe increases the bioavailability of P (Liptzin and Silver, 2009), which is often
476 sorbed to Fe(III)-(hydr)oxides in soil and saprolite.

477 We can estimate the flux of Fe into the extractable reservoir due to hornblende
478 weathering using Equation 5. The gradient, b_s , in total Fe(II) across the zone of hornblende
479 weathering, which occurs over 7 cm at the bedrock-rindlet interface, is $b_s = 0.088 \text{ m kg mol}^{-1}$

480 (Buss et al., 2008), $\phi = 0.063 \text{ g g}^{-1}$ (White et al., 1998), and $\rho = 1.83 \times 10^6 \text{ g m}^{-3}$ in the deep
481 saprolite (White et al., 1998). The resulting flux, $F_{Fe} = 4.5 \times 10^{-7} \text{ mol Fe m}^{-3} \text{ s}^{-1}$. This rate of
482 input can be compared to the rate of output via goethite crystallization using Equation 5 and the
483 gradient in extractable Fe in the deep saprolite, $b_s = 19.01 \text{ m kg mol}^{-1}$ (Figure 4b), and $\phi =$
484 0.0018 g g^{-1} (Buss et al., 2005). The resulting Fe flux out, $-F_{Fe} = 7.3 \times 10^{-8} \text{ mol Fe m}^{-3} \text{ s}^{-1}$, is an
485 order of magnitude slower than the Fe flux in due to hornblende dissolution. This result is
486 consistent with the observation that the extractable reservoir reaches the isotopic value of the
487 middle saprolite before (at $\sim 4.6 \text{ m}$ depth) it reaches the concentration value of the middle
488 saprolite (at $\sim 4.0 \text{ m}$ depth).

489 Enhanced dissolution of hornblende by organic ligands, suggested by the isotopic and
490 concentration gradients in extractable Fe at the bedrock-saprolite interface, indicates an active
491 role for biota in chemical weathering. In addition to increasing the rate of hornblende dissolution,
492 organic ligands produced by microorganisms may increase the rate of other mineral weathering
493 reactions by lowering the pH of the porefluids. Furthermore, microbial consumption of oxygen
494 during respiration may affect the rate of spheroidal fracturing, which is thought to be controlled
495 by the concentration of oxygen in the porewater (Fletcher et al., 2006). These results raise the
496 possibility of a “bio-limited” weathering profile in which a change in the rate of biogeochemical
497 weathering would lead to a change in the total denudation rate. Weathering systems are typically
498 classified as either weathering-limited or transport-limited (Stallard, 1992; Kump et al., 2000;
499 Riebe et al., 2004; West et al., 2005). In a weathering-limited regime, total denudation is
500 controlled by the chemical weathering rate, which is limited by the kinetics of mineral
501 weathering reactions. In contrast, in a transport-limited regime (also called supply-limited), the
502 total denudation rate is controlled by the rate of erosion. In the transport-limited case,

503 perturbations in the weathering rate do not affect the total denudation rate because the
504 weathering rate is high relative to the erosion rate; development of a thick regolith is a
505 consequence. Because the Rio Icacos weathering profile is consistent with models of transport-
506 limitation (Fletcher et al., 2006; Lebedeva et al., 2007), it is unlikely that microbial influence on
507 the weathering rate would affect the denudation rate or the thickness of the regolith profile
508 studied here. However, it is interesting to note that a weathering-limited profile could also be
509 bio-limited.

510

511 **5. Conclusions**

512 Iron in HCl extracts of saprolite samples is slightly fractionated relative to igneous rocks
513 through the majority of a saprolite profile overlying quartz diorite in the Luquillo Mountains,
514 Puerto Rico: $\delta^{56}\text{Fe}$ values generally range from approximately 0 to -0.1 ‰. However, HCl-
515 extractable Fe is significantly enriched in the lighter isotope in samples taken from the soil and
516 from the bottom of the saprolite directly overlying the bedrock, where $\delta^{56}\text{Fe} = -0.64$ and -
517 0.40‰, respectively. These zones of lighter Fe isotopic compositions are consistent with the
518 zones of highest biological activity in the saprolite as measured by cell density. Whereas
519 organisms in the soil are generally heterotrophic and can thrive on relatively abundant organic
520 carbon in the soil and porewaters, little to no organic carbon is available at the bedrock-saprolite
521 interface, other than cellular material. Microorganisms at the bottom of the saprolite therefore
522 rely on Fe and P released from the spheroidally weathering bedrock as an energy and nutrient
523 source, respectively, with Fe as the limiting “nutrient”. The bedrock-saprolite interface is
524 characterized by spheroidal fractures that delineate ~2.5 cm-thick rindlets and that comprise ~50

525 cm thick rindlet sets. Apatite is present in the corestone at parent abundance, but is not measured
526 in the saprolite: we calculate that apatite weathers across the rindlet sets at a rate of 6.8×10^{-14}
527 $\text{mol m}^{-2} \text{s}^{-1}$. Using growth yields from the literature and weathering release rates of Fe(II),
528 biomass production rates were calculated previously by Buss et al. (2005). The apatite
529 dissolution rate calculated here produces a flux of P sufficient to support these growth rates.
530 Therefore our results suggest that P is not limiting at the saprolite-bedrock interface. These
531 results are consistent with the conclusion, advanced in our earlier paper, that the ecosystem that
532 survives at ~5 m depth in the saprolite directly above the bedrock in the Rio Icaos weathering
533 profile is dependent upon chemolithoautotrophic primary producers. These chemolithoautotrophs
534 are Fe(II) oxidizers and are sustained through Fe released from the weathering bedrock. Active
535 cycling of Fe by microorganisms is reflected in the isotopically light Fe in the HCl extracts from
536 the top and bottom of the weathering profile, although the cycling and fractionation mechanisms
537 may differ between the surface and deep ecosystems. The preferential mobilization of light Fe
538 isotopes at the bedrock-saprolite interface suggests that microorganisms are likely influencing
539 concentrations of Fe and oxygen in the porewater and thus affecting the rates of weathering of
540 Fe-bearing minerals.

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Table 1.
Apatite content of rindlets and corestone

Distance¹ (cm)	Apatite² (vol %)
49.0	nd ³
48.5	nd
48.0	nd
47.5	0.01
33.0	0.14
30.0	nd
28.0	nd
21.0	0.20
16.0	0.35
8.5	0.38
5.0	0.11
4.0	0.36
0	0.62

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¹ Distance from corestone

² Determined by point counting
backscattered electron images of thin
sections using image analysis software.

³ nd = not detected

Table 2.
Fe isotope ratios of HCl extracts

Depth (m)	$\delta^{56}\text{Fe}$ (‰)
0.15	-0.64
0.3	-0.66
0.6	-0.55
0.9	-0.13
1.2	-0.26
2.1	-0.12
2.4	-0.08
2.4	-0.11
3.0	0.00
3.7	-0.11
4.3	-0.10
4.6	0.01
4.9	-0.40

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798 **Figure Captions**

799 **Figure 1.**

800 Solid-state, Ti-normalized concentrations of P, C_w , with depth in the weathering profile that was
801 sampled by augering on a ridgetop. The dashed line denotes the bottom of the saprolite. Samples
802 below the saprolite were inferred to be rindlet-zone samples on the basis of texture, color, and
803 chemistry. Error is the standard deviation of the measured concentrations of P for five individual
804 samples of a single corestone. The higher concentrations at ~2.5 m correspond to a visible,
805 chemical, textural, and biological heterogeneity identified by Buss et al. (2005) as a “ghost
806 rindlet”.

807

808 **Figure 2.**

809 Solid state, Ti-normalized concentrations of P, C_w , in the rindlet and corestone samples collected
810 from a roadcut (open triangles). The left-hand y-axis shows the distance below the saprolite-
811 rindlet interface. A linear fit through the roadcut data is shown, which was used as the gradient in
812 P, b_s , for calculation of the apatite weathering rate and P flux (Equations 3 and 5). The equation
813 for the regression line is $Y = 36.3X - 0.13$, $R^2 = 0.76$. Error bars are the standard deviation of the
814 measured concentrations of P for five individual samples of a single corestone. Solid square
815 symbols are C_w for P in the rindlet zone portion of the augered core (Figure 1) corresponding to
816 the right-hand y-axis, which shows the depth in the augered core.

817

818 **Figure 3.**

819 Backscattered Electron (BSE) image of a thin section of a rindlet from about 4 cm above the
820 corestone sampled in a road cut. The remnants of a dissolving apatite crystal are visible within an

821 apatite-shaped hole. While apatite weathers across the entire 49 cm rindlet zone, hornblende only
822 weathers within 7 cm at the saprolite-rindlet interface (Buss et al., 2008). The sample in this
823 image is below the zone of hornblende weathering and thus the hornblende crystal appears
824 pristine.

825

826 **Figure 4.**

827 **a)** Isotopic composition of Fe extracted with 0.5 N HCl from the soil and saprolite samples. Error
828 is $2\sigma = 0.1\%$ calculated for multiple measurements of a goethite standard. **b)** Fe concentrations
829 in 0.5 N HCl extracts (Buss et al., 2005) with a linear regression through concentrations at depths
830 below 4 m representing the gradient in extractable Fe over this zone. Error bars are smaller than
831 most of the symbols. **c)** Cell numbers estimated by direct counting (Buss et al., 2005), and **d)** cell
832 numbers estimated from DNA yields (Buss et al., 2005). Notice the log scale for the cell
833 numbers in c-d. The anomalously high cell density at ~2.2 m in c corresponds to a relatively
834 unweathered zone in the saprolite, thought to be a “ghost rindlet” (Buss et al., 2005).

835

836 **Figure 5.**

837 Rates of apatite dissolution determined from laboratory experiments (Valsami-Jones et al., 1998;
838 Welch et al., 2002; Guidry and Mackenzie, 2003, Schaperdoth et al. Unpub.) show a linear
839 dependence on pH (Bandstra et al., 2008). The field rate determined in the present study is
840 several orders of magnitude slower than the laboratory rates. Laboratory rates are normalized to
841 BET surface area of the mineral. The field rate is normalized to a geometric mineral surface area.
842 The field pH of 5.4 was measured by White et al. (1998) in porewater on the Guaba Ridge.