**Feedbacks among O₂ and CO₂ in deep soil gas, oxidation of ferrous minerals, and fractures:
a hypothesis for steady-state regolith thickness**

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21 Abstract

22 O₂ and CO₂, the two essential reactants in weathering along with water and minerals, are
23 important in deep regolith development because they diffuse to weathering fronts at depth. We
24 monitored the dynamics of these gas concentrations in the hand-augerable zone on three
25 ridgetops—one on granite and two on diabase—in Virginia (VA) and Pennsylvania (PA), U.S.A.
26 and related the gas chemistry to regolith development. The VA granite and the PA diabase
27 protoliths were more deeply weathered than the VA diabase. We attribute this to high protolith
28 fracture density. The pO₂ and pCO₂ measurements of these more fractured sites displayed the
29 characteristics of aerobic respiration year round. In contrast, the relation of pO₂ versus pCO₂ on
30 the more massive VA diabase is consistent with seasonal changes in the dominant electron
31 acceptor from O₂ to Fe(III), likely regulated by the expansion/contraction of nontronite in the
32 soil BC horizon. These observations suggest that the fracture density is a first order control on
33 deep regolith gas chemistry. However, fractures can be present in protolith but also can be
34 caused by oxidation of ferrous minerals. We propose that subsurface pO₂ and weathering-
35 induced fracturing can create positive feedbacks in some lithologies that cause regolith to thicken
36 while nonetheless maintaining aerobic respiration at depth. In contrast, in the absence of
37 weathering-induced fracturing and depletion of pO₂, a negative feedback that may be modulated
38 by soil micro-biota ultimately results in thin regolith. These feedbacks may have been important
39 in weathering systems over much of earth's history.

1. Introduction

The balance between erosion and weathering at depth defines the thickness of regolith—defined here as the physically, chemically, and biologically altered material on top of protolith. These processes are subject to feedbacks which may result in a steady-state regolith thickness. For instance, as soil thickens, the effects of surface processes such as bioturbation become weaker, effectively isolating the soil-bedrock interface. Consequently, the soil production rate can decrease under thick regolith (e.g., Heimsath et al., 1997). In thicker regolith, feedbacks between surface and subsurface processes may be mediated primarily by chemical reactions (e.g., Behrens et al., 2015; Fletcher et al., 2006; Fletcher and Brantley, 2010; Heimsath et al., 2012) because water and gas can infiltrate to the bottom of regolith and promote weathering. Hence, if the erosion rate increases at the surface because of changing climate or other factors, thinner regolith will allow more reactive waters to reach protolith, increasing the rate of weathering front propagation at depth (Fletcher et al., 2006).

Among chemical processes, the oxidation of ferrous minerals (e.g., biotite, pyroxene) may play a critical role in propagating the weathering front. Oxidation can increase the overall volume of the mineral assemblage, eventually rupturing the rock (Bazilevskaya et al., 2015; Behrens et al., 2015; Brantley and Olsen, 2013; Buss et al., 2008; Fletcher et al., 2006; Navarre-Sitchler et al., 2015; Røyne et al., 2008; Rudge et al., 2010). These fractures then become new conduits to advect reactive water to incipiently weathering bedrock, resulting in new fractures. Such weathering-induced fracturing (WIF) may increase the propagation rate of the weathering front (e.g., Fletcher et al., 2006; Røyne et al., 2008); in consequence, regolith becomes thicker. Indeed,

Bazilevskaya et al. (2013) demonstrated that regolith on granite ridgetops is thicker than that on diabase under similar climate regimes. They then inferred from modeling that such differences can be attributed to differences in mechanisms of solute transport in granite and diabase caused by presence or absence of WIF.

The significance of WIF likely depends on the content of ferrous minerals in protolith and the availability of O_2 at depth. Although some previous studies have considered dissolved O_2 in soil pore water (e.g., Fletcher et al., 2006; Røyne et al., 2008), a few recent studies have proposed that gaseous O_2 may also play a central role in regulating the surface-subsurface feedback (Behrens et al., 2015) and overall regolith thickness (Brantley et al., 2014). O_2 comprises 21 % (v/v) of ambient air and can passively diffuse into soil. Brantley et al. (2014) proposed that when the ratio of O_2 to CO_2 (R') in the soil atmosphere is greater than the capacity of protolith minerals to consume O_2 (e.g., the concentration of ferrous minerals) versus CO_2 (e.g., plagioclase), R'^0 , weathering would induce fracturing and create thick regolith. However, these studies were based strictly on solid (i.e., soil and bedrock) chemistry rather than soil gas chemistry.

The dynamics of O_2 in deep regolith, in fact, has received little attention. Most soil gas studies have focused only on CO_2 in the soil layer. Furthermore, except for a few studies (e.g., Bacon and Keller, 1998; Davidson and Trumbore, 1995; Johnson et al., 2008; Richter and Markewitz, 1995; Schwendenmann and Veldkamp, 2006; Wood and Petraitis, 1984), soil gas observations have been restricted to the top ~1 m, where O_2 can freely diffuse. These studies thus have generally assumed the dominance of aerobic respiration. O_2 has been monitored in low- O_2

settings such as wetlands, peat, or tropical rainforests (e.g., Elberling et al., 2011; Silver et al., 1999); however, direct observations of the gas composition, for both O₂ and CO₂, of the zone below the soil layer (i.e., saprolite and weathered bedrock zone) have rarely been documented.

To understand the role of regolith gas chemistry on the oxidation of ferrous minerals and the evolution of the critical zone structure, direct observations of O₂ and CO₂ dynamics in regolith are essential. Thus, in this study, we monitored the concentrations of gaseous O₂ (pO₂) and CO₂ (pCO₂) in the hand-augerable zone (mostly saprolite) on two end-member lithologies. Specifically, we study protolith with differing Fe content i.e., diabase (Fe(II)-rich) and granite (Fe(III)-poor) weathering profiles in ridgetops in Virginia. We studied an additional diabase profile in Pennsylvania that was more fractured than the Virginia diabase. Our study was designed to explore the dynamics of regolith gas chemistry with respect to the importance of Fe content (VA diabase vs. VA granite) and fracturing (VA diabase vs. PA diabase). We report pO₂ and pCO₂ time-series measured at a bi-weekly interval over two years at three sites. We also report stable isotope measurements (i.e., ¹³C-CO₂ and ¹⁸O-O₂). In comparison to previous studies of the geochemistry of these sites, our observations elucidate the role of gas in regolith development.

2. Background

The study sites are located in the Valley and Ridge physiographic province (PA diabase) and the Piedmont region (VA granite and VA diabase; Figure 1a). Previous studies have extensively

102 investigated the geochemical properties of the study sites or nearby systems (Bazilevskaya et al.,
103 2015, 2013; Brantley et al., 2014; Hausrath et al., 2011; Pavich et al., 1989). For example,
104 Pavich et al. (1989) extracted core samples from land surface to protolith at local ridge tops of
105 the two rock types in the Piedmont region in Virginia and reported comprehensive geochemical
106 properties. As a continuation of these previous studies, we selected our study sites to be as close
107 as possible to theirs (Figure 1b and 1c). Our soil and saprolite samples were highly comparable
108 to the previous studies' findings; thus we describe the major characteristics of the study profiles
109 by synthesizing with theirs.

110 Our study sites share similar geologic history and modern landscape features. These landscapes
111 have been weathered for hundreds of millions of years (Table 1) and are thus considered to be at
112 a geomorphic steady-state. Today's Piedmont landscape is comprised of gently rolling hills that
113 are eroding slowly (e.g., 4–13 m·Myr⁻¹; Pavich et al., 1985; Reuter, 2004; Table 1). Porosity,
114 total carbon, and chemical depletion generally increase upward (Figure 2). The chemical
115 alteration, expressed by the normalized elemental mass transfer coefficient for individual
116 elements (τ ; Anderson et al., 2002), varies from -1 (100 % depletion) to 0 (0 % depletion) to
117 positive values (enrichment). Near the soil-saprolite interface, the clay contents sharply increase
118 in all three sites, indicating the formation of a pedogenic BC soil horizon (Figure 2). Our sites
119 are covered temperate broadleaf and mixed forest, which is approximately 80 years old, but are
120 surrounded by moderately developed areas (i.e., residential or agricultural).

121 While the soil layers were consistently thin (< 1 m), the total regolith thicknesses vary
122 significantly from site to site (Figure 2). For example, the depth to hand-auger refusal at our site

was measured at -7.2 m on the VA granite. In comparison, Pavich et al. (1989) reported that depths to protolith on granite in this region varied between -15 to -30 m. They also reported that regolith depth on the Occoquan granite in a borehole drilled ~5 km south of our site (F11 in Figure 1c) was -22 m. Based on this, we assume that the depth to bedrock on our site is roughly the same.

The depths of hand-auger refusal of the diabase sites were much shallower than the VA granite but differed between the sites: -3.8 m (PA) versus -1.4 m (VA; Figure 2). Furthermore, the PA diabase may be spheroidally weathered; spheroidally weathered corestones (diameter 0.9–1.8 m) were observed in a quarry on the same diabase formation that is located approximately 50 km south to the site (Hausrath et al., 2011). In contrast, the VA diabase protolith is massive and showed no evidence of spheroidal weathering. Bazilevskaya et al. (2013) reported that outcrops of the diabase observed in a quarry next to the site (Figure 1) showed an average of 7.2 ± 2.6 macro-fractures ($> 3 \mu\text{m}$ diameter pores) per m^2 and nanoporosity $< 2 \%$. Pavich et al. (1989) documented a wide range of regolith thickness (0–10 m; average 6 m) on diabase in the VA Piedmont. Consistent with this, one of their diabase boreholes adjacent to our study site (F18 in Figure 1c) showed thin regolith (-1.4 m) while others were weathered deeper along joints and faults, developing spheroidal corestones. We attribute such differences in these two diabase sites to the initial fracture density. In general, dikes have better developed jointing than sills in the Piedmont (Roberts, 1928). In addition, dikes such as the PA diabase are expected to be finer-grained than sills such as the VA diabase. We have previously argued that the high fracture density in the PA diabase may lead to WIF and spheroidal weathering (Brantley et al., 2016).

The two diabase protoliths displayed similar mineralogical compositions (Bazilevskaya et al., 2015, 2013; Hausrath et al., 2011; Pavich et al., 1989): the dominant primary minerals were Ca-rich feldspar (i.e., bytownite or labradorite) and pyroxene (i.e., augite); the dominant secondary minerals were Fe-rich smectite (i.e., nontronite), Al-oxides, and Fe-oxides; and the weathering-resistant minerals such as quartz and mica were negligible (Table 1). The total Fe and Fe(II) contents of the protolith were around 10–11 and 7.8–10 % (w/w), respectively. In contrast, in the VA granite, quartz and plagioclase were the most abundant primary minerals, followed by muscovite, K-feldspar, and biotite in order of decreasing abundance (Table 1). The secondary minerals were kaolinite with minor Fe-oxides and vermiculite. The VA granite's total Fe and Fe(II) contents were 2 and 1.6 % (w/w), respectively.

The mineralogical differences may cause these two lithologies to develop distinct features in weathering profiles (Bazilevskaya et al., 2013; Brantley et al., 2014). First, reaction fronts of plagioclase—the depth interval over which Na, Ca-feldspar concentrations change due to weathering—are much wider on the VA granite (~ 10 m) than on the VA diabase (~ 0.2 m). The τ_{Na} and τ_{Ca} profiles of the two sites illustrate such differences (Figure 2). Second, the oxidation front (i.e., the depth where $\tau_{\text{Fe(II)}}$ returns to 0) is much deeper than the acid-dissolution front (i.e., where τ_{Na} returns to 0) on the VA granite. In contrast, these two fronts are almost coincident on the VA diabase. Bazilevskaya et al. (2013) used the F11 and F18 core samples collected by Pavich et al. to show that the biotite oxidation front is in the weathered bedrock zone (~ -22.5 m) on the VA granite, whereas the plagioclase dissolution front extends from the saprolite to weathered bedrock zones (-12.5 to -20 m). Conversely, on the VA diabase, both augite and plagioclase dissolution fronts were thin (~ 10s cm) and co-located at the saprolite-weathered

bedrock interface (~ -1 m). The authors also identified micro-fractures around the oxidized biotite grains in the F11 unweathered granite samples. In contrast, they did not observe signs of oxidation in the deep F18 diabase samples: instead, the dissolution of ferrous lamellae in augite without oxide precipitation was observed.

3. Method

3.1. Subsurface gas observations

The pO_2 and pCO_2 in the regolith were monitored at a ridge-top at each study site bi-weekly since May 2014 (Figure 1a). The sampling campaign at the PA diabase was terminated around March 2015 but sampling is ongoing at the other two sites. Detailed sampling protocol and analysis methods can be found in the supplementary material. Gas was withdrawn from gas access tubes installed at various depths, mostly in the saprolite zone (Figure 2), using a 60 mL syringe. Prior to sampling, the sampler was purged with approximately 60 mL of air. The samples were injected into a pre-evacuated 12 mL Labco® vials with a septa closure. Each sample was over-pressurized by hand (> 40 mL of gas sample). All the gas samples were analyzed for pCO_2 and pO_2 generally within a month, after ascertaining that the sample vials maintained the initial high pressure. Selected sets of the VA samples were analyzed for $^{13}C-CO_2$ and $^{18}O-O_2$.

3.3. Oxidation Ratio

The oxidation ratio is defined here as the stoichiometric ratio of O_2 consumed to CO_2 produced for a reaction. Angert et al. (2015) showed that the oxidation ratio can be estimated from statistical analysis of pO_2 and pCO_2 measurements. Here, we assume O_2 diffuses in from the top, and is consumed as it moves down. In contrast, CO_2 is produced at depth and is consumed as it diffuses upward. The slope of a plot of O_2 (y-axis) versus CO_2 (x-axis) for all depths documents the oxidation ratio for the regolith and its y-intercept indicates the initial pO_2 concentration. For a soil open to the atmosphere, the y-intercept will equal atmospheric pO_2 .

Here we make two assumptions that are tested below: i) O_2 and CO_2 are coupled and the oxidation ratio reveals the stoichiometry of the controlling reaction(s); and ii) that the relative diffusivity of O_2 with respect to CO_2 is constant with depth. If the first assumption is valid, pO_2 and pCO_2 should show a strong linear relationship, as discussed below. In terms of the second assumption, it is well known that O_2 diffuses faster than CO_2 : the diffusion coefficient of O_2 in free-air, D_{O_2} , is $0.182 \text{ mol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ while that of CO_2 , D_{CO_2} , is $0.138 \text{ mol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ (Angert et al., 2015). The apparent diffusion coefficient of CO_2 (or O_2) in soil i.e., D'_{CO_2} (D'_{O_2}), must be corrected for porosity (ϕ) and air content (ϕ_a ; Hendry et al., 2002; Millington and Quirk, 1961):

$$D'_{O_2} = \frac{\phi_a^{\frac{7}{3}}}{\phi^2} D_{O_2} \quad (1)$$

$$D'_{CO_2} = \frac{\phi_a^{\frac{7}{3}}}{\phi^2} D_{CO_2} \quad (2)$$

203 Thus, the second assumption is valid because both diffusivities vary with the same correction
204 factor.

205 To estimate the oxidation ratio for the studied systems, thus, we estimated the best-fit linear
206 equation for all pO_2 versus pCO_2 data for each site (Eqn. 3):

$$207 \quad pO_2 = a pCO_2 + b \quad (3)$$

208 Then the oxidation ratio was determined by the corrected slope, a^* that is the product of the
209 slope a and D_{O_2}/D_{CO_2} (Angert et al., 2015):

$$210 \quad a^* = \frac{0.182}{0.138} a = 1.32a \quad (4)$$

211

212 4. Results

213 4.1.1. Observations

214 4.1. 1 PA diabase

215 In the PA diabase, pCO_2 increased (0.04 to 6.1 %) and pO_2 decreased (20.9 to 14.6 %) with
216 increasing depth, with little seasonal variation (Figures 2 and 3). These concentration changes
217 occurred mostly in the upper 1.25 m. Below this depth to the bottom of the profile (-3.8 m),

218 pCO₂ and pO₂ remained constant. pO₂ and pCO₂ of the PA diabase showed a strong linear
219 relationship with a slope of -0.94 ± 0.03 ($R^2 = 0.82$; Figure 4a). The y-intercept, 20.63 ± 0.17 , is
220 consistent with the known value for ambient pO₂.

221 4.1.2 VA granite

222 As in the PA diabase, pCO₂ generally increased (0.1 to 10.7 %) and pO₂ decreased (20.9 to
223 6.4 %) with increasing depth (Figure 2). The VA granite gas chemistry displayed slight temporal
224 variation in the shallow zone (~ -0.5 m) while concentrations became relatively invariant below -
225 2 m (Figure 2 - 4). pO₂ and pCO₂ were clustered around a line with a slope of -0.96 ± 0.03 and a
226 y-intercept of 20.56 ± 0.15 ($R^2 = 0.77$; Figure. 4b).

227 4.1.3 VA diabase

228 In the VA diabase, pCO₂ increased and pO₂ decreased with increasing depth (Figure 2); however,
229 in contrast to the other sites, this site exhibited strong seasonality over the two years of
230 observation (Figure 2–4). In the late summer and fall, pCO₂ and pO₂ profiles were similar to
231 those of the other two sites: from the surface to -1.4 m, pCO₂ increased from 0.3 to 1.9% and
232 pO₂ decreased from 20.1 to 17.7 % with increasing depth. In contrast, during the winter and
233 spring, pCO₂ and pO₂ showed the largest changes from the ground surface to -0.5 m. Below this
234 depth, pCO₂ was lower and pO₂ higher than the values at -0.5 m. For example, from April to
235 May 2015, pCO₂ averaged 3.6 % (at -0.5 m) and 2.7 % (< -0.5 m), and pO₂ averaged 9.18 % (at -
236 0.5 m) and 10.3 % (< -0.5 m). As the summer proceeded, pCO₂ started to decrease as pO₂
237 increased.

In Figure 4c, the VA diabase manifested this seasonality as a counter-clockwise loop over time, especially for measurements deeper than -0.5 m (Table 2). From August to September, pO_2 and pCO_2 were somewhat scattered but are nonetheless consistent with a slope of -0.85 ± 0.4 and a y-intercept of 21.8 ± 0.7 . As the fall proceeded to winter, the slope and y-intercept started to decrease, indicating that O_2 was consumed at a higher rate than CO_2 was produced relative to that of aerobic respiration. From March to May, pO_2 and pCO_2 in this zone were strongly correlated, showing a slope of -2.68 ± 0.12 and a y-intercept of 18.5 ± 0.3 . As the summer began, the slope started to increase again and eventually returned to -1.

4.2. Stable isotopes

$\delta^{13}C-CO_2$ at the VA sites varied within the range reported for typical soil CO_2 in temperate forests (-11 to -25 ‰; Figure 5a and 5c; Amundson et al., 1998). The y-intercepts of plots of $\delta^{13}C-CO_2$ vs. $1/pCO_2$ of the VA sites were around -24.66 ‰, which is slightly depleted compared to CO_2 derived from decomposition of C3 plants (average C3 plants' $\delta^{13}C = -27$ ‰ ; Amundson et al., 1998) after accounting for kinetic fractionation (+4.4 ‰). The $\delta^{13}C$ of ambient air (-11 ‰) was also slightly depleted compared to the global average value (-8 ‰ ; Amundson et al., 1998). This slight depletion is attributed to anthropogenic sources such as car emissions which lower local ambient $\delta^{13}C$ values below the global atmospheric average. The deeper samples of the VA granite and the winter samples of the VA diabase were enriched in ^{13}C compared to the mixing line between ambient and biologically respired CO_2 (red boxes in Figure 5a and 5c).

The $\delta^{18}\text{O}-\text{O}_2$ of the VA sites increased as their pO_2 decreased (Figure 5b and 5d), indicating preferential removal of the lighter isotope (^{16}O) compared to the heavier one. The ambient air was slightly enriched in $\delta^{18}\text{O}$ —i.e., +31.78 ‰ (VA granite) and +30.5 ‰ (VA diabase)—compared to the global average (+23.5 ‰; Wassenaar and Hendry, 2007). For samples with similar pO_2 in the VA granite, samples displayed higher $\delta^{18}\text{O}$ values in late summer than in winter/spring (Figure 5b). For example, at -6 m, pO_2 ranged from 12.1 % (Dec.) to 13.8 % (July), while $\delta^{18}\text{O}$ values were much lower in December (+32.0 ‰) than July (+47.89 ‰). The negative correlation between $\delta^{18}\text{O}$ and pO_2 was most clearly demonstrated in the VA diabase (Figure 5d). The most enriched signature ($\sim +69$ ‰) was observed in May when pO_2 was lowest (9.4 %).

6. Discussion

6.1. Controls for seasonality of the VA diabase regolith gas

Although all three sites were weathering in a similar climate, seasonal changes in gas chemistry were observed only in the VA diabase (Figure 4). The seasonality thus cannot be explained solely by climate conditions such as freeze-thaw or snow cover. However, seasonal changes were synchronized with the net average water content inferred from precipitation (P) minus potential evapotranspiration (PET) for the site (Table 2; NCED, NOAA 1964 - 2015). Precipitation is evenly distributed throughout the year for the VA sites but PET, estimated from the monthly average air temperature using the Thornthwaite equation (Thornthwaite, 1948),

278 varies seasonally. During the moist conditions of the winter and spring, $P > PET$ and the y-
279 intercept ranged from 18.5 to 19.7 %. In contrast, during the summer and early fall when $P <$
280 PET , the y-intercept increased back to 21.8 %.

281 Given these observations, we propose that during the wet season, oxygen becomes depleted in
282 the VA diabase regolith as the soil moisture increases. One explanation for this could be ferrous
283 mineral oxidation but it is also likely that the nontronite in the BC horizon expands and plugs
284 fractures and pores. For such a plugged horizon, water perches, effectively limiting the gas and
285 water exchange between the ambient air and the saprolite/weathered bedrock zones. By the end
286 of the summer, however, when the system is at its driest condition, nontronite likely contracts
287 and the pores in this BC horizon open for gas exchange. The high $\delta^{18}O$ in the VA diabase
288 during the wet season is consistent with this isolated system explanation (Figure 5). As spring
289 commences and the evapotranspiration rate increases, the isotope signatures of soil water
290 become enriched. O_2 gas in regolith may equilibrate with this enriched soil water, driving its
291 $\delta^{18}O$ value more positive.

292 Such seasonality was not observed in the PA diabase and VA granite, although a BC horizon at
293 each site was detected as well (Figure 2). In the VA granite, the dominant secondary mineral is
294 kaolinite, which is not expandable. Therefore as soil moisture increases, gas will diffuse more
295 slowly; however, fractures will not become sealed. In addition, the granite has a lower
296 concentration of ferrous minerals thus oxygen depletion is less likely. In contrast, in the PA
297 diabase, the predominant clay is also nontronite and ferrous minerals are abundant. However,
298 the smaller grain size and denser fracturing of this dike protolith apparently precludes plugging

by the nontronite. We infer that the PA diabase and VA granite operate as open systems year round while the VA diabase operates as an isolated system during the wet season.

6.2. The dominant metabolism in the isolated system

Under open conditions, we have argued that the differences in gas diffusivity must be considered using Eqn. 4 to interpret the oxidation ratio. However, under the isolated conditions that occur in the VA diabase in the wet season, diffusion effects may be negligible because gas exchange between the surface and subsurface is limited. Furthermore, pO_2 and pCO_2 of the isolated zone display no variation with depth (Figure 3). In this case, the bulk regolith gas must be well mixed in these deeper layers. Therefore, the oxidation ratio under isolated condition should be inferred from the slope of the pO_2 - pCO_2 relationships without making the diffusion correction.

The pO_2 and pCO_2 of the VA diabase under isolated conditions showed a strong linear relationship, which was reproduced over the study period. This consistency indicates that biogeochemical reactions other than aerobic respiration control the regolith gas during the wet season. Apparently, as nontronite swells and oxygen is depleted by reactions with ferrous minerals, microsites below the BC horizon or within clay aggregates can become anaerobic, even though the bulk regolith gas still displays moderately high pO_2 (7 to 10 %). Indeed, various laboratory experiments and field observations have demonstrated that such spatial heterogeneity is commonly observed and plays a key role in the cycles of redox-sensitive elements such as Fe, N, Cr (e.g., Dubinsky et al., 2010; Fimmen et al., 2008; Masue-Slowey et al., 2011; Sexstone et

al., 1985; Tokunaga et al., 2001). For example, Sexstone et al. (1985) directly measured pO_2 in the interior of soil aggregates of radius 4 to 10 mm that were incubated in ambient air. They showed that pO_2 rapidly decreased with increasing distance from the aggregate surface and eventually became negligible at 3~6 mm depths. Consistent with this, Dubinsky et al. (2010) showed that Fe oxidizers and reducers coexist in tropical soils where the average pO_2 ranged between 8 to 21 % (Silver et al., 1999). They also reported a positive correlation between the Fe(II) production rate and the abundance of Fe oxidizing bacteria. Apparently, Fe oxidizing and reducing bacteria are mutually dependent.

In the VA diabase, during the winter when the wet season begins, O_2 diffusion from the atmosphere may slow down due to expansion of nontronite, and O_2 may drop because of consumption of O_2 by aerobic respiration and augite oxidation. These effects may explain the decrease of pO_2 without significant changes in pCO_2 during the early wet season (Figure 4c). As the wet season proceeds, anaerobic micro-sites may become fully developed, and the Fe(III) in nontronite may start to become reduced via dissimilatory Fe-reducing bacteria (Lovley and Phillips, 1988; Roden, 2006; Roden and Zachara, 1996; Eqn 5a). A simple version of this reaction can be expressed as follows:

Although reductive dissolution of nontronite can be more complicated than Eqn. 5a, no attempt was made to match the exact stoichiometry of the reaction. Calculations for the weathered

bedrock zone by Bazilevskaya et al. (2015) showed that Fe(II) became depleted without significant precipitation of Fe(III) oxides, consistent with loss of Fe(II) under reduced conditions. Diffusion of Fe(II) to the aerobic micro-sites may also lead to oxidation back to mixed Fe(II)/(III) oxides such as magnetite (Fe₃O₄; Eqn. 5b):

Fe(III) can also be reduced via abiotic carbon mineralization of phenolic substances (e.g., Pracht et al., 2001) and Fe(II) can be oxidized to other than magnetite. These variations will yield different $\Delta\text{O}_2/\Delta\text{CO}_2$ ratios; however, the coupling of the first two reactions (Eqn. 5a and 5b) yields $\Delta\text{O}_2/\Delta\text{CO}_2 = -2.67:1$ (Eqn.6), which is nearly identical to our observations (Table 2):

Therefore, we propose that these coupled Fe redox reactions may explain the slope of the pO₂-pCO₂ relationship for the VA diabase under isolated conditions.

These observations demonstrate the importance of parallel measurements of pO₂ and pCO₂. For example, pO₂ under the isolated condition was still moderately high; thus without measurements of pCO₂ it might have been tempting to conclude that Fe reduction was not possible in the regolith. However, both geochemistry and gas chemistry observations are consistent with the importance of coupled dissimilatory Fe(III) reduction and Fe(II) oxidation in the VA diabase

regolith. We propose that the relationship between pO_2 and pCO_2 —rather than their absolute concentrations—provides more insight into the dynamics of the deep regolith environment and controlling metabolic processes for regolith gas chemistry.

6.3. The third CO_2 end-member

In Figure 5, atmospheric CO_2 ($\delta^{13}C-CO_2 = -11\text{‰}$) and biologically respired CO_2 ($\delta^{13}C-CO_2 = -24.66\text{‰}$) can be clearly inferred as end-members. We also identified a second mixing line for some VA granite samples (i.e., deeper depths year-round and shallower depths during the spring) and for the VA diabase samples in winter. These observations imply a contribution of a third end-member. We therefore hypothesize that either ^{13}C of soil organic carbon (SOC) varies with depth; or dissolution/precipitation of calcite contributes to the regolith gas pCO_2 .

When SOC is decomposed, ^{12}C is preferentially released as CO_2 ; consequently, old SOC tends to be more enriched in ^{13}C than fresh SOC (Wynn, 2007). If a pool of older SOC at depth is significant, then the respired CO_2 might be enriched in ^{13}C compared to that derived from the fresher carbon sources. However, in all three sites, the total carbon contents were negligible below -1 m ($< 0.01\%$ w/w; Figure 2). Thus we exclude this hypothesis.

The second hypothesis provides a more feasible explanation. For example, Bazilevskaya et al. (2015) detected calcite at the saprolite-weathered rock boundary, near the plagioclase (An06) weathering front (-19 m) in the VA granite (0.14 % w/w) and at the weathered-fresh bedrock

boundary near the augite weathering front (-0.9 m) in the VA diabase (2.25 % w/w). Based on these observations, the authors concluded that dissolution of primary Ca-containing minerals released Ca^{2+} ions to solution at those depths, causing calcite precipitation. The ^{13}C of this calcite was not measured; however, at equilibrium at 10°C, calcite is enriched in ^{13}C compared to gaseous CO_2 by +9.18 ‰ (Emrich et al., 1970). Therefore the newly precipitated calcite is likely to be enriched in ^{13}C compared to regolith gas and re-dissolution of this calcite could therefore affect the isotope signature of the pCO_2 . Thus we propose that the third end-member for the ^{13}C vs. pCO_2 mixing lines may be inorganic C in calcite.

7. Implications

7.1. Feedback between O_2 and fracture propagation

Bazilevskaya et al. (2013) compiled global regolith data and showed that regolith developed at ridgetops underlain by granite are, on average, five times thicker than those on diabase in regions where $P > \text{PET}$. Paradoxically, dissolution rates of the most abundant mineral in mafic rocks (Ca-rich feldspar) are faster than those in felsic rocks (Na-rich feldspar; Bazilevskaya et al., 2013). These puzzling observations could be explained in various ways. For example, Pavich et al. (1989) proposed that a higher fraction of intergrowths of the relatively insoluble minerals such as quartz and mica in granite than that in diabase could sustain the regolith's structural integrity, allowing thicker regolith to form. In contrast, in diabase, such insoluble minerals are rare. Therefore, regolith in mafic rocks is expected to be thin if collapse occurs after dissolution.

Alternatively, Buol and Weed (1991) proposed that during pedogenesis, a layer of low hydraulic conductivity (i.e., the BC horizon) between soil and saprolite develops and prevents percolation of meteoric water to deeper zones, eventually slowing saprolite weathering. They argue that the pedogenic smectite-rich BC horizon on diabase acts as an “armoring layer”, preventing weathering at depth. Finally, Bazilevskaya et al. (2013, 2015) and Brantley et al. (2014) showed with numerical models that regolith is thicker wherever solute transport is dominated by advection as opposed to diffusion. They argued that advective transport was more likely on granitic than on mafic diabase because WIF is more prevalent on the more felsic lithology.

Building upon our soil gas observations and aforementioned studies, we propose that both positive and negative feedbacks between gas chemistry and fracture density in regolith contribute to the differences in regolith thickness between mafic and felsic rocks (Figure 6). For protolith that is relatively Fe-poor (i.e., granite) or fractured (i.e., PA diabase), oxidation occurs deeper than acid-promoted dissolution; then WIF occurs. Volume expansion by oxidation outcompetes production of porosity by dissolution at depth, causing fracturing. These fractures allow rapid communication between the surface and the deep subsurface, maintaining high pO_2 at depth and fostering aerobic respiration. This positive feedback between pO_2 and WIF promotes advective transport of solutes and therefore may lead to the development of thick regolith (Figure 6a). As Pavich et al. (1989) proposed, the structural integrity of weathered granite also is likely to contribute to keeping high pO_2 at depth as well.

Conversely, for Fe-rich and massive rocks (i.e., VA diabase) where oxidation is not the deepest alteration reaction because O_2 becomes depleted at shallow depths, WIF is less likely to occur.

In these systems, pO_2 in the regolith is low because (1) expansion/contraction of the nontronite-rich BC horizon isolates the deep regolith, limiting O_2 supply; and (2) biotic and abiotic Fe oxidation consume O_2 intensely: diabase contains high Fe(II) and biotic Fe redox cycles consumes more O_2 per a given carbon source than aerobic respiration does. Such arguments can adequately explain why oxidation of augite at depth in the incipiently weathering VA diabase was observed to be insignificant (Bazilevskaya et al., 2013, 2015). This explanation amplifies and expands upon the Buol and Weed hypothesis. The negative feedback as shown in Figure 6c may be responsible for thin regolith on the VA diabase.

These feedbacks imply the role of WIF in regolith development is a function of both Fe(II) content in protolith and O_2 availability. For instance, if a protolith contains too little Fe(II), then WIF will still occur but may negligibly increase permeability of rocks. Conversely, for high Fe(II) protolith, O_2 can become significantly depleted at depth due to the oxidation of ferrous minerals and biotic O_2 consumption in the shallower depth. Here we emphasize that soil biota may play a key role in these feedbacks, particularly in facilitating the negative feedback, by controlling the O_2 availability at depth.

7.2. Key processes controlling weathering fronts at the fresh bedrock boundary

For a better understanding of the evolution of landscape and critical zone architecture, the processes that are responsible for defining the bottom of the weathering profile must be understood. Despite its importance, however, the controlling mechanism for this bottom

boundary is still rarely investigated. At least three processes have been proposed that control this lower boundary. First, Rempe and Dietrich (2014) proposed that the fresh bedrock boundary (Z_b) coincides with a no-flow boundary: meteoric water effectively does not infiltrate below it. The authors argue that as the stream channel near a ridge incises, it creates lateral hydraulic gradients; consequently, the groundwater slowly drains out of the hillslopes to the stream. This desaturated fresh bedrock then weathers (e.g., wetting-drying). The authors termed this a bottom-up model. Second, St. Clair et al. (2015) hypothesize that the interaction between regional tectonic compressive stress and topographic stress may open fractures at depth under hills. These fractures then serve as conduits for meteoric water to infiltrate at depth, driving subsequent weathering. The third mechanism is coupled reactive transport, where weathering advance is caused by advection or diffusion of solutes to the weathering front, which can be in turn affected by the rate of erosion at the land surface (Lebedeva et al., 2010, 2007; Lebedeva and Brantley, 2013).

In this study, we propose that WIF—mediated by a mixture of water and gas transport processes coupled to biogeochemical reactions—may play an important role in demarcating the fresh bedrock boundary under ridgetops particularly in slowly eroding landscapes underlain by crystalline rocks. Our work also emphasizes that the interactions among several underlying mechanisms may be responsible for weathering front propagation. For instance, as we mentioned earlier, the PA diabase may be more fractured than the VA diabase because of differences related to emplacement as a dike vs. a sill. We argue that this difference may ultimately be responsible for the higher O_2 at depth in the PA site compared to the VA diabase, which in turn may facilitate WIF (Buss et al., 2008; Fletcher et al., 2006). Thus, the PA diabase

is weathered deeper with spheroidal weathering patterns. Collectively, the differences in the initial conditions between the PA and VA diabase may lead to different weathering processes and ultimately result in the differences in the regolith thicknesses.

These mechanisms also operate in parallel or as coupled behaviors. For example, when meteoric water is perched on a fresh bedrock surface, water may not infiltrate but oxygen molecules can diffuse—even though it might be slow—below this boundary, promoting WIF. These new fractures will increase the permeability of this oxidized zone. Consequently, groundwater in this zone drains out, lowering the groundwater table and propagating the oxidation-front. However, as the bottom-up model proposes, channel incision also drops the groundwater table. The bottom-up model proposes that protolith will be desaturated first and will be followed by weathering as a secondary process while the WIF model proposes that weathering will turn protolith to regolith and then desaturation will occur.

It is possible that actively eroding sedimentary systems are more susceptible to fracturing by wetting-drying than crystalline rocks; therefore, they may commonly operate as bottom-up controlled landscapes. Indeed, Rempe and Dietrich evaluated their model mainly in such landscapes (i.e., erosion rates = 100-400 m Myr⁻¹). Conversely, slow eroding landscapes underlain by crystalline rocks such as near level landforms of the Piedmont may be more representative of the WIF-controlled landscapes. Indeed, the differences in regolith thickness that are observed in the same erosion regimes between granite and diabase cannot be explained solely by the bottom-up model. In the future, the propagation rate of weathering fronts by WIF must be quantified for various climatic and lithologic conditions to compare the relative

importance of various earth surface processes. Such comparisons may contribute to our understanding of the evolution of the earth surface environment and may allow development of predictive models of landscape evolution.

8. Conclusion

Regolith gas chemistry was monitored at three locations underlain by Fe-rich (i.e., diabase) and Fe-poor (i.e., granite) rock types in Virginia (VA granite and VA diabase) and Pennsylvania (PA diabase) for two years. In the VA granite and PA diabase, pre-existing (i.e., faults and joints) or weathering-induced fractures allowed communication between the surface and subsurface environments. Thus, the O₂ availability even at several meters below the land surface was maintained high enough to enable aerobic respiration year-round. Such high O₂ availability was likely to explain the observed weathering-induced fracturing which acts like a positive feedback in driving further deep oxidation. We propose this feedback is necessary to maintain thick regolith in slowly eroding systems underlain by crystalline rocks.

In contrast, in the massive VA diabase, both the lack of macro-fractures and the high Fe content of the protolith led to development of a nontronite-rich BC horizon that controls the connectivity between the surface and subsurface. The VA diabase gas chemistry showed strong seasonality synchronized with wetting and drying of the BC horizon. In the wet season, the nontronite in the BC horizon swelled, isolating the deep regolith. Under this isolated condition, O₂ became limited because O₂ is not replenished while the biotic Fe redox cycling consumes O₂ intensely.

In the dry season, as the nontronite dried and contracted, the deep regolith became re-connected to the surface environment. Then aerobic respiration again controlled the regolith gas chemistry. Because of this seasonal O₂ limitation, augite dissolves in the deep regolith without oxidative precipitation of ferric minerals; therefore, weathering-induced fracturing apparently did not occur in the deep VA diabase. Without new fracturing, in this massive rock, diffusion may remain the only transport mechanism for reactive solutes, keeping O₂ low. We propose that this negative feedback contributes to the thin regolith of this diabase. Importantly, biota may play a key role in modulating this loop by rapidly depleting O₂ at depth.

Overall, we propose that in slow-weathering systems under similar climate regimes, fractures may be a first order control to determine the regolith thickness. Fractures facilitate supply of O₂ which in turn drives oxidation and fracturing at depth. Without the deep fractures as observed in the granite, weathering apparently did not drive oxidation in the diabase, resulting in thin regolith. In contrast, when weathering-induced fracturing occurs, the Fe-poor rock (granite) develops deeper regolith than the Fe-rich rock (diabase). Further research is needed to assess this latter difference and to numerically simulate our conceptual model.

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Figure 1. Overview of the study sites. The subsurface gas was monitored at three locations at ridge top positions underlain by two different lithologies: PA diabase; VA granite and VA diabase. (a) The PA diabase is in the Ridge and Valley Ridge physiographic province and the VA sites are in the Piedmont region. (b) The PA diabase is located at a narrow dike. Hausrath et al (2011) investigated geochemical properties of the hand-augured soil samples at the same locations of this study. The authors also observed spheroidally weathered outcrops in a local quarry (light blue triangle). (c) Both the VA granite and VA diabase are located in Fairfax County, Virginia. The physical and geochemical properties of weathering profiles on the granite (F11) and diabase (F18 and F19) were extensively investigated by Pavich et al., (1989) and Bazilevskaya et al., (2013, 2015). They also characterized the geochemical properties of unweathered bedrock using outcrops from local quarries.

Figure 2. Summary of subsurface physico-chemical properties (porosity, total carbon content, texture, τ_{Ca} , τ_{Na} , $\tau_{Fe(III)}$, $\tau_{total Fe}$), gas well installation, monthly averaged pCO₂ and pO₂ in PA diabase (top), VA granite (mid), and VA diabase (bottom). At each site, 10-12 gas wells were installed; however, over the monitoring period, some wells had been clogged likely by the translocation of clay minerals. *The depths to the weathered and unweathered bedrock are from the core data interpretation of Pavich et al., (1989).

Figure 3. Time series of precipitation, daily maximum and minimum air temperature, pO₂, pCO₂, and ΔpO₂/ΔpCO₂ (from the atmospheric levels) of PA diabase (top), VA granite (bottom left), and VA diabase (bottom right). The color of the pO₂ and pCO₂ markers changes from blue for ambient (pO₂=22%; pCO₂ = 0%) to red for aerobically respired compositions (pO₂ = 15%; pCO₂ = 7%). Thus, when the color of pO₂ and pCO₂ are similar, this indicates that O₂ is consumed and CO₂ is produced at a -1:1 ratio, i.e., as expected if this chemical reaction is occurring: $\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$. When the colors of the gases are different, the ratio is different and aerobic respiration may not be a dominant process.

Figure 4. Observed pO_2 vs. pCO_2 of (a) PA diabase, (b) VA granite, and (c) VA diabase. The shapes and colors of markers represent the sampling depths and months, respectively.

Figure 5. $\delta^{13}\text{C}$ vs. $1/p\text{CO}_2$ and $\delta^{18}\text{O}$ vs. $p\text{O}_2$ of (a and b, respectively) VA granite and (c and d, respectively) VA diabase. The red boxes of the $\delta^{13}\text{C}$ plots are the zoom-in view of the low $1/p\text{CO}_2$ (high $p\text{CO}_2$) ranges. The color and shapes of the markers are consistent to those of Figure 4.

Figure 6. Feedback loops between O_2 availability and weathering induced fracturing (WIF). (a) In felsic rocks, the positive feedback between O_2 and WIF may contribute to developing thick regolith, i.e., VA granite. (b) The positive feedback is feasible in mafic rocks if there are pre-existing fractures, which allow rapid replenishment of water, solute, and gas to depth. Therefore, mafic rock can develop moderately thick regolith, i.e., PA diabase. (c) In unfractured mafic rocks, WIF does not generally occur. Seasonal swelling/shrinking of smectite isolates the deeper zone and limits O_2 supply at depth. Consequently, the deeper zone becomes reduced and ferrous minerals are dissolved, not oxidized. This negative feedback may play a critical role in developing thinner regolith on mafic rocks.

Table 1. Summary descriptions of study sites

	PA diabase	VA granite	VA diabase
geology			
Lat. Long.	40° 11' 21.96" N, 77° 6' 27.29" W	38° 45' 13.78" N, 77° 16' 34.47" W	38° 49' 58.68" N, 77° 29' 20.93" W
lithology	diabase	granite	diabase
age	200Ma	450Ma	200Ma
hand- augur refusal	3.8 m	7.2 m	1.4 m
depth to fresh bedrock	?	22 m	1.4 m
erosion rate	12-19 mm kyr ⁻¹	4-13 mm kyr ⁻¹	4-13 mm kyr ⁻¹
soil type	Alfisol	Ultisol	Alfisol
mineralogy			
primary mineral in fresh bedrock	bytownite (An60-90)> augite>> magnetite> ≈ ilmenite ≈ apatite	quartz > plagioclase (An6) > K-feldspar >> muscovite ≈biotite	labradorite (An50-70) > augite >> K-feldspar ≈ ilmenite ≈ magnetite
secondary mineral in regolith	Fe-rich smectite (nontronite), kaolinite/chlorite, goethite	kaolinite, minor Fe-oxides, vermiculite	Fe-rich smectite (nontronite), Fe-oxides, Al-oxides
Fe (II) in fresh bedrock (% w/w)	10.14	1.45	7.8
total Fe in fresh bedrock (% w/w)	11.27	1.77	10.1
climate			
Climate type	humid continental	humid subtropical	
mean annual precipitation (mm yr ⁻¹)	1146	1049	
mean annual temperature (°C)	11.5 (-6.6 ~ 30)	12.6 (-4 ~ 29)	

Table 2. Long-term average of monthly precipitation, potential evapotranspiration, and net water budget (P-PET) in the VA sites and slopes and y-intercepts of pO_2 versus pCO_2 in the zone below -0.5m on the VA diabase

	VA sites water budget			VA diabase below 0.5m [^]		
	P [†]	PET [‡]	P-PET	$pCO_2 = a pO_2 + b$		
				<i>a</i>	<i>b</i>	<i>R</i> ²
Jan	60	0	60	-2.32	19.7	0.58
Feb	76	2	74	±0.5	±1.1	
Mar	74	19	54	-2.67	18.5	0.94
April	69	50	19	±0.12	±0.3	
May	105	91	14			
June	123	129	-7	-1.27	19.8	0.30
July	89	152	-63	±0.6	±3.2	
August	108	136	-28	-0.89	21.8	0.69
Sept	80	93	-12	±0.2	±0.7	
Oct	85	48	37	-1.38	20.79	0.43
Nov	84	20	64	±0.18	±0.3	
Dec	95	4	91			
Sum	1047	744	303			

[†] NCED, NOAA land-based station data measured at Dulles Airport, VA (1964 – 2014)

[‡] Potential evapotranspiration estimated from using the Thornthwaite equation (Thornthwaite 1948). For the PET calculation, the same NCED data set (Dulles Airport, VA) as the precipitation was used.

[^] Estimates based on this study's gas chemistry observations