Investigation of a Diabase-derived Regolith Profile from Pennsylvania: Mineralogy, Chemistry and Fe Isotope Fractionation

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Abstract:

At Earth's surface, bedrock transforms to regolith in a process that has many implications for water storage, soil formation, and nutrient availability to ecosystems. To understand deep regolith formation, we investigate three zones demarcating changes in mineralogy, chemistry and Fe isotopic composition in a 4-m thick regolith profile developed at a ridge top in Pennsylvania (U.S.A.) that is underlain entirely by diabase. Zone 1, at the bottom, is characterized by major element depletion, abrupt oxidation of Fe(II), a rapid decrease in sulfur concentrations and the presence of short-range ordered (SRO) Fe with depleted $\delta^{56}\text{Fe}$ values. We attribute many of the observations at this depth (which we refer to as the lithogenic zone) to the effects of spheroidal weathering, which may be releasing a flux of Fe(II) with low $\delta^{56}\text{Fe}$ values as the mineral pyroxene is weathered. This Fe(II) is oxidized and likely precipitated as isotopically light SRO Fe phases, which then recrystallize with time. Crystallization in Zone 2 is inferred to result in loss of isotopically light SRO Fe. Finally, SRO Fe isotopic compositions become lighter again near the land surface in Zone 3, the zone of most intense biogenic weathering related to exudation of protons and organic acids by plant roots. In this zone, these acids solubilize and remove isotopically light SRO Fe. This pattern of SRO Fe isotopic variability, which has been observed in other deep regolith profiles on spheroidally weathering bedrock, may be explained best by a combination of lithogenic and biogenic processes. The effects of biota reach deeper than the dominantly biogenic zone due to high concentrations of carbon dioxide, trapped in the soil by the low-permeability Bt/BC interface. Dissolution based on modern pore fluids in the upper two meters of regolith is occurring at a rate that is within an order of magnitude of the time-integrated rate of dissolution constrained mineralogically in the upper two meters. This correspondence is consistent with the conclusion that the rate of regolith formation remains roughly constant over time. Constant rates of weathering are expected in zones where erosion rates and rainfall are also constant. In that case, the thickness of the diabase may be considered to be at steady state (i.e., the rate of weathering advance due to deep lithogenic processes is roughly equivalent to the rate of advance at shallow depths due to biogenic processes).

Keywords: Fe isotopes; deep regolith; chemical weathering; diabase; spheroidal weathering; preferential flow

1. Introduction

Although the C horizon is often underemphasized in studies pertaining to soil weathering (Richter and Markewitz, 1995), important reactions occur deep within the regolith profile (Bazilevskaya et al., 2013; Buss et al., 2005; Minyard et al., 2012; White et al., 1998). While researchers have been studying reactions in deep regolith since the 1970s (e.g., Brimhall et al., 1992; Buol and Weed, 1991; Calvert et al., 1980a; Calvert et al., 1980b; Eswaran and Bin, 1978; Gardner et al., 1978; Gilkes and Suddhiprakan, 1979; Graham et al., 1989; Rice et al., 1985; Stolt et al., 1992), recent efforts are setting the stage for the quantitative interpretation of mineral weathering by probing reactions that occur near the bedrock-regolith interface. In deep regolith near the bedrock-regolith interface on siliceous rocks, one of the first reactions is Fe oxidation, which is followed by depletion of silicate minerals (e.g., Chigira and Oyama, 2000; Drake et al., 2009). In the Rio Icacos watershed of Puerto Rico, intense weathering of a quartz diorite results in the near complete loss of plagioclase, K-feldspar and hornblende at the bedrock-regolith interface that lies meters beneath the land surface (White et al., 1998). In contrast, Garnder et al. (1978) observed the gradual dissolution of plagioclase and biotite over the bottom few meters in a granite saprolite in South Carolina. At this interface, Buss et al. (2005; 2010) also noted oxidation of Fe that resulted in an increase in the abundance of short-range order (SRO) Fe along with notable changes in SRO Fe isotope signatures. Finally, Bazilevskaya et al. (2013) studied diabase and granite soil profiles in Virginia and reported distinct zones of Fe(II) oxidation and sulfur depletion near the bedrock-regolith interface. The goal of the current study is to investigate the regolith-bedrock interface of another system to ascertain whether deep weathering beneath a ridge top leads to specific patterns in mineralogy, solid-state and pore-water chemistry, and Fe isotopic composition.

The study site is a 4-m regolith profile developed on an oak-dominated ridge top underlain by diabase in central Pennsylvania (PA, U.S.A.). Diabase in Pennsylvania is present primarily as sills and dikes that occur in large swarms that can extend for kilometers (Mottana et al., 1977; Smith et al., 1975).

The primary silicate minerals in the PA diabase are plagioclase and augite, which weather to form smectite and kaolinite (Hausrath et al., 2011). Previous research suggests three distinct weathering zones (Hausrath et al., 2011). These zones occur 1) in the lowermost 50 cm of the profile above the bedrock-regolith interface, 2) in the middle of the profile, where elemental concentrations remain relatively constant with depth, and 3) in a zone extending from 0 to 150 cm below the land surface. As discussed herein, the first zone is inferred to be mostly “lithogenic” (dominated by rock + water + gas reactions), while Zone 3 is inferred to be “biogenic” (dominated by rock + water + gas + biotic reactions).

Several methods were used in this study to understand chemical changes in regolith with depth, including Fe isotope analysis of bulk and HCl-extracted Fe (inferred to remove SRO Fe), Fe(II) determinations in bulk regolith, X-ray diffraction (XRD) and transmission electron microscopy (TEM). Although many studies have analyzed Fe isotopic composition within soils (e.g., Akerman et al., 2014; Brantley et al., 2004; Buss et al., 2010; Emmanuel et al., 2005; Fantle and DePaolo, 2004; Fekiacova et al., 2013; Guelke et al., 2010; Mansfeldt et al., 2012; Poitrasson et al., 2008; Thompson et al., 2007; Wiederhold et al., 2007a; Wiederhold et al., 2007b; Yesavage et al., 2012), many questions remain. For instance, while some profiles show minimal isotopic variability in bulk Fe with depth, other profiles vary in systematic ways as a function of depth (Fekiacova et al. (2013) and references within). With respect to HCl-extractable (SRO) Fe, some studies indicate minimal fractionation between soil horizons (e.g., Poitrasson et al., 2008; Wiederhold et al., 2007a; Wiederhold et al., 2007b), while other studies indicate a significant extent of fractionation (Fantle and DePaolo, 2004; Wiederhold et al., 2007a). Moreover, while some studies have observed SRO Fe phases that have low $\delta^{56}\text{Fe}$ values relative to the bulk soil (Guelke et al., 2010; Wiederhold et al., 2007a; Wiederhold et al., 2007b; Yesavage et al., 2012), other profile horizons have secondary phases that have higher $\delta^{56}\text{Fe}$ values than bulk Fe (Fantle and DePaolo, 2004; Thompson et al., 2007). In the current study, samples were collected from a series of different depths from a site underlain entirely by diabase bedrock to yield an understanding of the bedrock-to-saprolite transformation as well as any isotopic changes taking place near the surface.

A part of this study also involved the measurement of pore-water chemistry (including cation and anion concentrations, pH, DOC concentrations and soil gas CO₂ concentrations) in the upper two zones to elucidate weathering processes. Although a wide variety of studies have examined temporal changes in DOC with depth in soils (Andrews et al., 2011; Dalva and Moore, 1991; Lorieri and Elsenbeer, 1997; Tolpeshta and Sokolova, 2009), fewer studies have examined other constituents including Al, Fe, Mn and nitrate (Asano et al., 2006; Avila et al., 1995; Dalva and Moore, 1991; Kowalska and Janek, 2009; Lorieri and Elsenbeer, 1997; Tolpeshta and Sokolova, 2009) or the effects of preferential flow paths (Andrews et al., 2011; Asano et al., 2006; Bundt et al., 2001). We use these measurements, as well as measured soil pore-water chemistry, to understand the formation processes of this regolith profile.

2. Methods

2.1. Study site

The study consists of a regolith profile underlain by a dike developed on the ca. 200 Ma Gettysburg diabase sheet (Mesozoic basin) (Sutter, 1988). Based upon evidence from a local quarry, this dike undergoes spheroidal weathering, with the largest corestones being ~2 m in diameter (Hausrath et al., 2011). The soil is mapped as the Neshaminy series, which is described as a deep, well-drained Alfisol formed from diabase and other dark-colored basic rocks (Soil Survey Staff, 2013). Previous work within the Appalachian mountain range indicates an erosion rate of ~5 mm/ky (references within Hausrath et al. (2011)).

2.2. Sample collection

Samples analyzed in the current study consist of Core 1 from Hausrath et al. (2011), which was collected in 2006 and analyzed for bulk chemistry, mineralogy and water content. This core was collected at intervals of ~10 cm and then subsequently air dried at room temperature, powdered with a Spex Shatterbox (model 8510) and stored at room temperature for several years. To avoid contributions from downslope mass movements, samples were collected from a forested ridge-top site at a location along the

Appalachian Trail (40°13'14.0"N/77°6'14.2"W) (Fig. 1). The site lies off the trail and is not currently highly disturbed by human impact. A four-inch diameter stainless steel hand auger was used to collect samples as a function of depth (see Hausrath et al. (2011) for details), with the bedrock-regolith interface defined as the depth of auger refusal. An additional core (not analyzed here) was sampled in the spring of 2013 to identify soil horizons (Table 1). Although diabase boulders are occasionally observed at the land surface, few if any outcrops of diabase are observed near the regolith profile site. Instead, samples of largely unweathered rock, inferred to be similar to the parent lithology, were collected from a nearby roadcut along the Pennsylvania Turnpike (40°13'16.0"N/77°6'11.2"W). Previous analysis of the bedrock sampled along the turnpike (Hausrath et al., 2011) revealed the following mineralogy based on Energy Dispersive Spectroscopy on polished sections (in volume %): 66% plagioclase (bytownite) ($\text{Ca}_{0.7}\text{Na}_{0.3}\text{Al}_{1.7}\text{Si}_{2.3}\text{O}_8$), 24% augite ($\text{Ca}_{0.33}\text{Mg}_{2.67}\text{Fe}_{0.33}\text{Si}_{3.01}\text{Al}_{0.99}\text{O}_{1.0}((\text{OH})_2)$), 5% magnetite and other Fe oxides and 1% ilmenite (FeTiO_3).

2.3. Chemical analysis

Elemental concentrations of soil samples as a function of depth were previously determined based on XRF analysis (Hausrath et al., 2011). Concentrations of ferrous Fe (wt. %) in soils were determined using a method that involves boiling 1 g of soil in the presence of HF and sulfuric acid and titrating with potassium dichromate (Goldich, 1984). Precision for this analysis was estimated to be better than $\pm 10\%$ based upon triplicate measurements on individual samples (Table 2). Total sulfur (S) concentrations were determined with a LECO Sulfur Analyzer (see Brantley et al. (2013a) for further details regarding method).

2.3. Pore-water sampling

To sample soil pore waters, porous cup tension lysimeters (Soil Moisture Inc., 1900 and 1920 F1 Series) were installed in November 2010 at depths of 15, 60, 95 and 125 cm. Lysimeters were preconditioned by washing with dilute nitric acid (10%) overnight and then rinsing in deionized water before installation. Each hole was augered to the desired depth, and a 2-mm sieve was used to

disaggregate soil, which was then added back into the hole in the same order in which it was removed. Another lysimeter was installed at 205 cm in April of 2013. These lysimeters consist of a ceramic cup with 1.3- μ m pores through which soil water is drawn with the creation of a vacuum in the lysimeter tube. To avoid disturbances associated with zero-tension lysimeter installation (Currie et al., 1996), sample collection did not commence until Fall 2011, although the deepest lysimeter was sampled within a couple of weeks of installation. One week prior to sampling, the lysimeters were pumped to -0.5 centibars; samples were then collected the following week using PVC tubing and plastic syringes. No samples were collected during the late summer due to dryness, nor during the winter due to sub-freezing temperatures.

In the field, a portable pH meter (Symphony SP70P) was calibrated daily and used to measure pH on all soil pore-water samples. Samples for cation and anion analysis were filtered and added to 15-mL metal-free Falcon tubes. For this study, dissolved cations were defined operationally as the fraction that passed through VWR International 25-mm (0.45- μ m pore size) Nylon syringe filters (North American Cat. No. 28145-489). To minimize precipitation, a few drops of Ultrex® Ultrapure HNO₃ from J.T. Baker were added to filtered samples on the day of collection. Cation concentrations were analyzed with inductively-coupled plasma atomic emission spectroscopy (ICP-AES, Perkin-Elmer ICP-AES 5300DV). DOC samples were filtered (<0.45 μ m), stored in combusted glass vials and acidified with HCl on the day of analysis. All water samples were stored in a refrigerator between sampling and analysis. DOC samples were measured with a Shimadzu TOC-5000A Analyzer. With this instrument, carbon in the sample is combusted to CO₂, which is detected with a non-dispersive infrared gas analyzer. Filtered anion concentrations of non-acidified samples were analyzed for chloride, fluoride, sulfate, phosphate and nitrate with a Dionex 2500 ICS under isocratic conditions and an eluent concentration of 39 nM KOH using an Ion Pac AS18 4 x 250 mm column and Ion Pac AG18 4 x 50 mm guard column.

The soil atmosphere was measured using the Stonestrom-style sampler method with some modifications (Stonestrom, 2006). After augering, stainless-steel gas samplers were placed at specific depths in the hand-augered hole and then back-filled with carbonate-free sand and capped above and

below with bentonite to seal off each individual gas sampler so that it collects gas from the assigned depth interval.

Soil gas samples were obtained by connecting a 60 mL gas-tight syringe to the sampler's three-way port and pulling a sample. To assure gas samples were representative of the depth of interest, the samplers were purged of air prior to sample collection so that no air from the above-ground portion of the sampler was collected. Gas samples were immediately transferred from the syringe with a needle to pre-evacuated 15-mL Labco® glass vials for longer storage before laboratory processing. The Labco® vials were overpressured (i.e., ≥ 40 mL of gas) to prevent contamination during storage. Soil gas CO₂ concentrations were analyzed in the laboratory by an infrared gas analyzer (IRGA; LI-7000, LI-COR Inc., Lincoln, NE). Instrument accuracy is 1% of the sample value. Sample runs were calibrated with 970 and 10300 $\mu\text{mol mol}^{-1}$ CO₂ standards (Gas and Technology Services Inc., Santa Maria, CA).

2.4. Microscopy and mineral identification methods

The clay-sized fractions of regolith samples from depths of 30, 70 and 340 cm were extracted by wet sieving and centrifugation (Jackson, 1956). Material was analyzed with TEM analysis on a Philips EM 420 TEM (120 kV). Samples were prepared by sonicating in ethanol and dispersing the solution onto a lacey carbon grid. Images and EDS data were collected from the sample in a Gatan double-tilt analytical holder with the holder inclined 30° in the x-axis.

XRD patterns were collected using a PANalytical Empyrean theta-theta style goniometer with Cu-K- α radiation, a fixed slit incidence (0.25° divergence, 0.5° anti-scatter, specimen length 10 mm) and diffraction optics (0.25° anti-scatter, 0.02 mm nickel filter). Regolith samples (sieved to $<100 \mu\text{m}$) were prepared by the back-loading method in which a powder sample is pressed into the cavity of a silicon low-background support. Clay-sized samples were prepared by the dropper method, which involves thoroughly suspending the sample in water and then dropping it on a glass slide (Whittig and Allardice, 1986). Data were collected at 45 kV and 40 mA from 5-70° 2 θ using a PIXcel detector in scanning mode

with a position sensitive detector (PSD) length of 3.35° 2 θ , and 255 active channels for a duration time of ~16 minutes. Resulting patterns were analyzed with Jade +9 software by MDI of Livermore, CA.

2.5. Sample digestion

All soils were digested in a perchloric acid hood, within a clean box. Prior to Fe isotope analysis, ~100 mg of air-dried bulk soil were digested at 90°C for 24 hours in acid-washed Savillex vials using a 1 mL: 3 mL mixture of HNO₃ (16 N): HF (29 N). One mL of concentrated perchloric acid (HClO₄, 11.6 N) was subsequently added to the dissolved sample, which was evaporated at 120°C until ~1 mL of solution remained, at which point the vessels were resealed and digested an additional 24 hours at 150°C. Samples were resuspended in 3:1:1 HNO₃ (16 N): HF (29 N): HCl (12 N), reacted for 2 hours at room temperature, sealed, and heated overnight at 150°C. Finally, samples were evaporated to dryness and redissolved in 0.5 N HNO₃. Even after addition of perchloric acid, samples containing large amounts of organic matter required up to 15 mL H₂O₂ to remove all visible organic matter. Upon removal of organic matter, samples were dried down in HNO₃ (16 N) to ensure oxidation of Fe and resuspended in 2 mL of 7 N HCl prior to ion exchange chemistry. All reagents used were ultrapure grade (e.g., Aristar®ultra HF, OmniTrace Ultra™ high purity HClO₄ and Ultrex® Ultrapure HCl, H₂O₂ and HNO₃ from J.T. Baker). Millipore 18.3 M Ω deionized water was used for all dilutions. Process blanks for the digestion procedure had Fe concentrations below the detection limit of ICP-AES of 50 ppb, about three orders of magnitude lower than Fe concentrations in digested samples.

To determine Fe redox state, 0.2 grams of sample were weighed into 15-mL metal-free tubes and 4 mL of 0.5 N HCl added. The tubes were then shaken on an end-over-end shaker for 24 hours at room temperature and centrifuged at 3,400 g for 15 minutes. The resulting supernatant was decanted and filtered through DI-rinsed 0.45- μ m VWR Nylon filters. The centrifugate was then washed with distilled water, centrifuged a second time, and the resulting supernatant filtered and combined with the first supernatant. The combined supernatant was then dried down on a hotplate and resuspended in 7 N HCl for Fe isotope analysis.

2.6. Iron isotope analysis

Iron has four naturally occurring isotopes: ^{54}Fe (5.85%), ^{56}Fe (91.75%), ^{57}Fe (2.12%) and ^{58}Fe (0.28%) (Dauphas and Rouxel, 2006). Variations among these isotopes are reported as $\delta^{56}\text{Fe}$ values (in permil, ‰, units):

$$\delta^{56}\text{Fe} = \left(\frac{\left(\frac{^{56}\text{Fe}}{^{54}\text{Fe}} \right)_{\text{sample}}}{\left(\frac{^{56}\text{Fe}}{^{54}\text{Fe}} \right)_{\text{std}}} - 1 \right) * 10^3 \quad (1)$$

The international Fe reference material IRMM-014 is used as a standard, which is ~0.09‰ lighter than average igneous rocks (Beard and Johnson, 2004a). The precision of $\delta^{56}\text{Fe}$ is generally reported at ± 0.05 to ± 0.15 ‰ (Beard and Johnson, 2004a).

Iron in all digested and extracted samples was chromatographically purified prior to isotopic analysis using BioRad's AG MP-1 anion exchange resin. Each column (bed volume = ~2 mL) was rinsed (7 mL 0.5 N HCl) and conditioned (9 mL 7 N HCl) prior to sample loading. Approximately 90 µg Fe in 7 N HCl was loaded onto each column, rinsed three times with 9 mL 7 N HCl, and the Fe eluted in 9 mL 0.5 N HCl. All Fe cuts were dried and resuspended in 0.45 N HNO₃. Yields were always >95%, as determined by analysis of aliquots of all sample solutions before and after column chemistry. Iron concentrations in post-column blanks were below the ICP-AES detection limit (50 ppb), which is two orders of magnitude lower than post-column sample concentrations.

Iron isotopic compositions were measured by multiple collector-inductively coupled plasma-mass spectrometry (MC-ICP-MS) using a Thermo Scientific Neptune Plus at Penn State University's Metal Isotope Laboratory (MIL). Samples were introduced using an ESI Stable Sample Introduction (SSI) quartz dual cyclonic spray chamber (i.e., under wet plasma conditions), either a 50 or 100 µl/min nebulizer flow rate (ESI PFA-50 or -100 microflow nebulizer), 1200 W power, standard Cu-cored Ni cones, and high mass resolution; laboratory room temperatures typically varied by less than 0.1°C/hr with

relative humidity controlled within a tolerance of $\pm 10\%$. All analyte solutions were matrix matched to the IRMM-014 bracketing standard (Fe concentrations = 3 ppm in 0.5 N nitric acid; ^{56}Fe beam intensities were between 10 and 19 V, depending on the analytical session and nebulizer used). Instrumental mass fractionation was corrected for by standard-sample-standard bracketing and resultant delta values reported relative to IRMM-014. All ion beams were collected in a single, static scan (integration time=8 sec, 35 cycles/analysis). Plateau tests conducted prior to the first analytical session determined the mass range over which the plateau was effectively flat, and all subsequent analyses were confined to this part of the plateau. Chromium was monitored at masses 52 and 53, and offline interference corrections applied for data quality purposes only. All $^{52}\text{Cr}/^{56}\text{Fe}$ ratios were below 0.00010, with an average value for all analyses of 0.000023 ± 0.000023 (1 SD). The data presented were analyzed over seven analytical sessions, with replicates analyzed across, as well as within, sessions. All analyses fall on the terrestrial mass fractionation line (Figure A.1).

Two inter-laboratory standards were run in each analytical session: NIST SRM-3126a ($\delta^{56}\text{Fe}_{\text{IRMM014}} = 0.34 \pm 0.10\%$ 2 SD, $n=12$; *accepted value*: 0.35%, personal comm., T. Bullen, 11-06-2012), and HPS-UW ($\delta^{56}\text{Fe}_{\text{IRMM014}} = 0.60 \pm 0.07\%$ 2 SD, $n=10$, *accepted value*: 0.58%, Beard et al., 2003). Single-element Fe standards from High-Purity StandardsTM were run before and after ion exchange separation to verify that column chemistry did not alter the isotopic composition of the samples; analysis of an Fe standard run before and after column chemistry yielded $\delta^{56}\text{Fe}$ values within 0.05%, thus demonstrating minimal fractionation due to column chemistry.

Poorly crystalline Fe oxides were extracted from previously powdered regolith (Hausrath et al., 2011) using 0.5 N HCl (Wiederhold et al., 2007a; 2007b). The HCl extractions are expected to liberate SRO and poorly crystalline Fe as well as aqueous Fe and weakly adsorbed Fe (Buss et al., 2010). We infer that most of the Fe oxides in this profile (derived from Fe(II) in pyroxene) are precipitated as SRO phases. Although magnetite is present in our sample, Kostka et al. (1994) showed that 0.5 N HCl extracted only ~1% of a standard magnetite sample over 24 hours (the same period of time that we used).

Consequently, even if magnetite makes up as much as half of all extracted SRO Fe, we would expect that no more than 0.5% of the total Fe in each sample would be extracted from the dissolution of magnetite by HCl. In contrast, the 0.5 N HCl extractions removed ~10% of the total amount of Fe from the samples (Table A.1). Beard and Johnson (2004b) observed minimal fractionation between magnetite and silicate minerals in four andesitic volcanic rocks. Based on six pyroxene-magnetite pairs from a tholeiitic Red Hill sill in Tasmania, Sossi et al. (2012) estimated an equilibrium fractionation factor of $\Delta^{57}\text{Fe}_{\text{mag-pyr}} \sim 0.3\text{‰}$ at 900-1,000°C. We would therefore not expect magnetite dissolution to significantly affect the HCl-extracted Fe isotope signature for this profile. Based on SEM images and EDS data, Hausrath et al. (2011) concluded that augite ($\text{Ca}_{0.33}\text{Mg}_{2.67}\text{Fe}_{0.33}\text{Si}_{2.01}\text{Al}_{0.99}\text{O}_{10}(\text{OH})_2$) makes up ~25% of the soil volume, while magnetite (Fe_3O_4) and other Fe oxides make up ~5%.

2.7. Mass balance geochemistry calculations

Plots of the mass transfer coefficient (τ_{ij}) in bulk soil samples were made to investigate the extent of chemical weathering. The τ_{ij} parameter is defined as (Brimhall and Dietrich, 1987; Anderson et al., 2002):

$$\tau_{i,j} = \frac{C_{j,w}C_{i,p}}{C_{j,p}C_{i,w}} - 1 \quad (2)$$

Here, C refers to the concentrations of the immobile (i) and mobile (j) elements in the weathered (w) or parent (p) material. Diabase bedrock collected from the Pennsylvania Turnpike was used as the parent material. Due to its insolubility, Zr appears to be the most immobile element at this site (Hausrath et al., 2011). The goal behind normalizing to an immobile element is to account for concentration changes in element j resulting from depletion and addition of other elements. Values of $\tau_{\text{Zr},j} > 0$ indicate that the element of interest (j) is enriched in soil relative to parent material, while $\tau_{\text{Zr},j} < 0$ indicates depletion or loss from the profile.

3. Results

3.1. Soil description

As reported by Hausrath et al. (2011), the depth of refusal based on hand augering was 401 cm. In 2013, we hand augered a second profile at the same site within 3 meters of the original profile to 395 cm for the purposes of identifying soil horizons. The following horizons were identified from the land surface downward (Table 1): A (0-22 cm), Bt (22-60 cm), BC (60-90 cm), Cr1 (90-160 cm), Cr2 (160-230 cm), Cr3 (230-340 cm), Cr4 (340-365 cm), Cr5 (365-395 cm), R (>395 cm). Notable horizon features include a strong brown (7.5YR 5/6) silty clay loam Bt horizon, which begins at 20 cm below surface and has a medium subangular blocky structure (Table 1). At a depth of ~60 cm, a transition is noted toward the yellowish brown (10YR 5/8) sandy loam of the BC horizon with a weak, medium subangular blocky structure. Also at the Bt/BC interface, distinct black manganese coatings (N 2.5/) are observed along ped faces and tubular pores. The Cr horizon is located between 0.9 to 4 meters and varies from olive yellow (2.5Y 6/6) sandy loam to strong brown (7.5YR 5/6) silt loam with an overall massive structure.

3.2. Trends in Fe and S chemistry with depth

Hausrath et al. (2011) reported major element depletion profiles for both in the lower 50 cm of the 4-m profile as well as in the upper 0-150 cm. In the current study, we observed that the percent of Fe present as Fe(II) decreases markedly from the value measured in parent material (83%) to the following values in deep regolith just above augering refusal: 56% at 401 cm and 12% at 379 cm (Table 2; Figure 2A). Although both total Fe and Fe(II) show losses of >80% over the entire profile, the overall depletion pattern differs. While Fe(II) is largely depleted toward the bottom of the profile, much of this Fe is retained at depth: the majority of the total Fe depletion occurs in the upper meter (Figure 2B). Sulfur concentrations throughout the regolith were about an order of magnitude lower than those of the bedrock (Table 2; Figure 2B).

3.3. Fe isotopic composition, XRD and microscopy

Bulk $\delta^{56}\text{Fe}$ values within the regolith average -0.04‰ , with minimal variations throughout the profile (Table 2; Fig. 3A). While bulk Fe $\delta^{56}\text{Fe}$ values throughout the regolith profile are within $\sim 0.1\text{‰}$ of the measured $\delta^{56}\text{Fe}$ of the diabase parent rock (-0.01‰), there is a slightly enriched $\delta^{56}\text{Fe}$ value at ~ 30 cm depth ($+0.1\text{‰}$) and a slightly depleted $\delta^{56}\text{Fe}$ value (-0.14‰) at 270 cm relative to parent. The $\delta^{56}\text{Fe}$ values of HCl-extracted regolith are about twice as variable as values observed in the bulk. Extracted regolith exhibits relatively light $\delta^{56}\text{Fe}$ values (-0.3‰) at the surface that transition to values near $\sim 0\text{‰}$ at intermediate depths that then return to depleted $\delta^{56}\text{Fe}$ values (-0.3‰) at depth near the bedrock-regolith interface (Fig. 3B).

X-ray diffraction analyses of clay-sized material extracted from the bulk regolith indicate the presence of a $14\text{ \AA}$ phyllosilicate mineral (smectite/vermiculite/chlorite), $7\text{ \AA}$ halloysite/kaolinite, and quartz. The $14\text{ \AA}$ phyllosilicate mineral was also present throughout the profile, whereas quartz was most abundant toward the surface of the profile (Figure 4). TEM images of the clay-sized fraction of diabase samples from three depths (30, 70 and 340 cm) show a variety of different morphologies (Figure 5A), including tube-like structures ~ 100 nm in diameter and up to $1\text{ }\mu\text{m}$ in length (Figure 5B). Transmission electron microscopy (TEM) diffraction patterns indicated that some of these tubes are short-range order while others are polycrystalline (Figures 5B and 5C). Rose-shaped morphologies that were SRO based on diffraction patterns were also noted. TEM/EDS analysis indicated that both the tubes and the rose-like structures were made up predominantly of Si and Al, with smaller amounts of Fe (Figure A.2), a composition consistent with both halloysite and newly-formed kaolinite (Papoulis et al., 2004).

3.4. Lysimeter chemistry

The pH of the pore water decreased from ~ 6.3 at the surface of the profile to ~ 5.6 at depth (Figure 6A; Table 3). This decrease in pH was accompanied by a corresponding increase in the percent of soil gas carbon dioxide (Figure 6B). The concentration of dissolved silica increased gradually from $\sim 10\text{ mg/L}$ at the surface to $\sim 30\text{ mg/L}$ at 205 cm (Figure 6C). In contrast, elements such as Mg, Na, K and Ca showed

greater variability and therefore less apparent trends with depth (Table 3; Table A.2). DOC concentrations ranged from 0 to 200 mg/L, and tended to decrease with depth, although with significant variation (Figure 6D). Nitrate concentrations ranged from 0-20 mg/L, with average values decreasing with depth (Figure 6E; Table 3). Despite variability, concentrations of dissolved Al and Fe were highest at a depth of 60 cm (Figures 6F and 6G). Indeed, pore water collected from 60 cm often was yellowish while waters were clear in color at all other depths. Chloride concentrations remained roughly constant with depth (Figure 6H). No significant differences were observed in the concentrations of DOC as a function of season. DOC concentrations were also not observed to be related to the amount of precipitation in the days and weeks prior to sample collection (Table A.3). Concentrations of DOC and nitrate are nonetheless more elevated in some years than others (i.e., higher concentrations in fall of 2011 and spring of 2012) (Figure A.3). DOC concentrations were well correlated with concentrations of Fe and K at the same sample depths, and moderately correlated with Al and Na ($p < 0.001$ in all cases).

4. Discussion

4.1. Fe cycling and isotopic effects associated with pedogenesis

Three zones of interest were investigated within the regolith profile at this site based on new observations and those from Hausrath et al. (2011) (Figures 2B and 7). Zone 1 (360-400 cm) is characterized by the onset of significant spheroidal weathering. In this zone, fractures in the diabase apparently allowed penetration of fluids that weathered the rock to initiate formation of rounded corestones (Hausrath et al., 2011). Total Fe (as well as Al, Ca, Mg, Mn, Si and Ti) was lost to about 20% depletion from this zone (Figure 2B; Hausrath et al., 2011). Similar to Buss et al. (2010), we observe isotopically light SRO Fe at this depth. If the dissolved Fe is isotopically light or if Fe that is precipitated is preferentially light, this can explain the isotopically depleted SRO Fe pool at these depths (Figure 3B). The rapid depletion of sulfur in this zone is attributed to the dissolution of pyrite near the bedrock-regolith

interface. In effect, this zone represents the initiation of weathering of the bedrock by oxidation of ferrous minerals including pyrite and pyroxene.

We interpret Zone 2 (150-360 cm) as the zone of ongoing spheroidal weathering that is characterized largely by the ripening and crystallization of SRO Fe phases as they age upward in the profile. Loss of total Fe and other elements from the bulk regolith is minimal in this zone (Figure 2B; Hausrath et al., 2011). Finally, Zone 3 (0 to 150 cm) appears to be a zone of total Fe and elemental loss from bulk soil (Figure 2B; Hausrath et al., 2011). The isotopically light SRO signatures in Zone 3 (0-150 cm) are attributed to mobilization and re-precipitation of Fe, most likely accelerated by exudates from vegetation in the upper 150 cm of the profile. These zones are discussed more completely in the next sections.

4.1.1. Zone 1: Control of soil Fe geochemistry by spheroidal weathering

The lowermost zone of the regolith profile (360-400 cm; referred to as Zone 1) is characterized by the onset of significant spheroidal weathering. This type of weathering was observed in diabase in a nearby quarry (Hausrath et al., 2011). In this zone, fractures in the diabase apparently allowed penetration of fluids that weathered the rock to initiate formation of rounded corestones. Fletcher et al. (2006) have argued that spheroidal weathering occurs when the diffusion of oxygen into bedrock along fractures initiates the oxidation of Fe(II) minerals. A volumetric increase accompanying oxidation then results in an elastic strain energy in the rock that creates a concentric set of rock layers (subtended by fractures referred to as rindlets) that slowly transform to the lowermost regolith (Fletcher et al., 2006).

As described by Hausrath et al. (2011), the variations in element concentrations with depth are attributed to the inward weathering of corestones--in other words, the weathering profile did not experience consistently increasing weathering upward due to the presence of the corestones. Despite this heterogeneity, we observe rapid oxidation of Fe(II) near the bedrock-regolith interface (Figure 2B). As spheroidal weathering occurs, we surmise that a flux of Fe(II) is released from the rindlets into the

lowermost regolith. Based upon XRD analysis of the bulk bedrock sample (Hausrath et al., 2011), most of this Fe(II) is derived from pyroxene (augite) and to a lesser extent, magnetite and ilmenite.

Bazilevskaya (2013) likewise noted a zone of Fe(II) oxidation in the lowermost 20 cm of a 100-cm thick regolith profile in Virginia regolith developed on diabase. For a nearby granite profile which was much deeper (~20 meters), a rapid Fe(II) oxidation front was also noted within close proximity to the bedrock-regolith interface (Bazilevskaya et al., 2013). Based on these observations as well as many other investigations (e.g., Chigira and Oyama, 2000; Drake et al., 2009; Jin et al., 2011), the transformation of bedrock to regolith may be initiated in many tropical and temperate locations by the onset of oxidation of ferrous iron-containing minerals.

On an area-normalized basis, the total mass of an element (j) lost or gained over a given depth in regolith can be expressed as (Brantley et al., 2013b):

$$m_j \approx \rho_p \int_{L_1}^{L_2} C_{j,p} \tau_{i,j}(x) dx \quad (3)$$

where ρ_p is density of parent material (~3 g cm⁻³ for the diabase), $C_{j,p}$ is the weight percent of element j in parent material (Table 2), $\tau_{i,j}(x)$ is the mass transfer coefficient for each depth increment (Equation 2) and dx is the depth increment. For the bottom 40 cm of the profile corresponding to Zone 1, we calculated that $m_{Fe(II)} = -840$ g cm⁻². In contrast, if all the Fe had been lost, then we would have expected a total Fe loss on the order of ~-1000 g cm⁻². On the contrary, $m_{total\ Fe} = -180$ g cm⁻², indicating a much smaller loss of total Fe. The most likely explanation for these values is that the majority of Fe(II) that is released during weathering at this depth is reprecipitated as ferric iron with only a small loss of ferrous Fe. This agrees with conclusions inferred for the VA diabase profile as well (Brantley et al., 2013b). Presumably this immobilized Fe is incorporated initially in some SRO form that matures into more crystalline phases from 360 to 400 cm.

Our observation of isotopically light SRO Fe was also made by Buss et al. (2010) in a Puerto Rico granodiorite (Figure 3B). In Zone 1, we attribute the light SRO Fe to dissolution reactions that preferentially mobilize isotopically light Fe during weathering that is then re-precipitated as isotopically light SRO Fe. It has been shown, for example, that proton-promoted dissolution at pH 4 releases Fe from biotite and chlorite that is isotopically lighter than the starting mineral (Kiczka et al., 2010a). Similarly, dissolution of hornblende releases isotopically light Fe into solution in the presence of microorganisms, organisms and siderophores (Brantley et al., 2001; Brantley et al., 2004). In fact, Buss et al. (2010) attributed isotopic depletion of SRO Fe in the Puerto Rico profile to re-precipitation of Fe released to solution by the organic-promoted dissolution of hornblende.

Although we refer to this deep zone of weathering as the lithogenic zone (White et al., 2006), we cannot rule out the impact of microbially-mediated Fe cycling. Ferrous Fe oxidation can be accelerated by bacteria living at the bedrock-regolith interface, even when that interface is on the order of a meter depth. For example, Minyard et al. (2012) used 16S rRNA clone libraries to document circumneutral Fe-oxidizing bacterial species living in the lower portion of the soil profile developed on quartz diorite in Puerto Rico. Minyard et al. (2012) argued that these microorganisms may contribute to loss of Fe(II) from the bedrock at the bedrock-saprolite interface. On the other hand, the abiotic oxidation of Fe(II) also proceeds rapidly under neutral pH conditions (Emerson et al., 2010). It is likely that both abiotic and biotic Fe oxidation occurs at depth in the Pennsylvania regolith wherever microorganisms have colonized. However, Fe-oxidizing bacteria are unlikely to explain the pattern of isotopically light amorphous Fe isotope fractionation because circumneutral Fe-oxidizing bacteria in batch studies have been observed to precipitate Fe oxides that are up to 3‰ *heavier* than the starting Fe(II) in solution (Kappler et al., 2010).

Zone 1 is also characterized by very low sulfur concentrations relative to the bedrock. Sulfur concentrations in the bottom of the regolith profile are an order of magnitude lower than in the parent material (Figure 2B). Sulfide in the Pennsylvania diabase occurs as pyrite grains, discrete grains of chalcopyrite and blebs of pyrrhotite and chalcopyrite (Smith et al., 1975). We attribute these observations

to the process of sulfide oxidation at a depth greater than the depth of refusal for hand augering. In a study of a drilled core from regolith on diabase in Virginia, for example, Bazilevskaya et al. (2013) observed rapid sulfide oxidation within 0.5 meters of the bedrock-saprolite interface. Given the similarities between the two sites, we conclude that both iron and sulfide oxidation are occurring at the bedrock-regolith interface. Most of the Fe is re-precipitated, while sulfur is presumably solubilized and lost from the regolith. Given the low porosity of the massive diabase, the depth of the water table at the Pennsylvania site is presumed coincident with the bedrock-regolith interface. Oxidation of Fe sulfide minerals is therefore likely to occur in a narrow zone near the water table.

4.1.2. Zone 2: Crystallization of SRO Fe phases

In general, the middle zone of the profile has regolith material that has been weathering longer than deeper regolith. We interpret the middle section of the profile as a zone in which Fe oxides formed at the bedrock-regolith interface mature to more crystalline phases. As weathering proceeds, processes such as dissimilatory Fe reduction and ligand-promoted dissolution of the SRO Fe likely release isotopically light Fe into solution (Beard et al., 1999; Brantley et al., 2001; Brantley et al., 2004), thereby explaining the SRO pool in this zone that is isotopically heavier than the Fe near the bedrock-regolith interface. Unlike Zones 1 and 3, concentrations of major elements (relative to Zr) stay constant within this ~2-m intermediate zone (Hausrath et al., 2011).

4.1.3. Zone 3: Effects of vegetation

Previous work suggests that Zone 3 is a region of major element depletion, which was attributed to increased concentrations of organic acids and to lower soil pH (Hausrath et al., 2011). Due to the higher abundance of plant roots and bacteria, elevated concentrations of organic ligands are expected in the surface horizons, once again releasing Fe into solution and causing precipitation of SRO phases. Alternatively, plants also tend to exude protons, which can further enhance weathering (Kiczka et al., 2010b). Given this emphasized importance of biotic processes, we term this zone the biogenic zone

(White et al., 2002). Similar to the results of Buss et al. (2010) for a graniodiorte-derived prolife in Puerto Rico, isotopically light SRO Fe toward the surface was observed. Previous work has demonstrated that plant material tends to be isotopically light relative to parent material for many types of plants, documenting that Fe mobilized by plant exudates is isotopically light (Guelke and von Blanckenburg, 2007; Guelke et al., 2010; Kickza et al., 2010b). These observations likely explain isotopically light SRO Fe in this zone in Pennsylvania and Puerto Rico.

4.2. Minimal isotopic fractionation of bulk Fe

While the Fe isotopic compositions of bulk igneous rocks tend to cluster around 0‰ (Beard and Johnson, 2004a), soils often show a greater variability in isotopic composition. For instance, the range of $\delta^{56}\text{Fe}$ values measured for bulk Fe in a variety of soil samples is $\sim 1.5\text{‰}$ (Wiederhold et al., 2007a). Many pedogenic processes may contribute to the isotopic fractionation of Fe relative to parent rock. For instance, mineral incubation experiments indicate that ligands preferentially release isotopically light Fe into solution relative to the starting material during the early stages of dissolution (Brantley et al., 2001; Brantley et al., 2004; Chapman et al., 2009; Kiczka et al., 2010a; Liermann et al., 2011; Wiederhold et al., 2006). Bacterially-mediated reductive dissolution may also cause Fe isotopic fractionation. For example, dissimilatory iron reduction of Fe (oxyhydr)oxides occurs when microorganisms use Fe(III) as an electron acceptor, resulting in the release of isotopically light Fe into solution (Beard et al., 1999). Finally, inorganic reactions such as precipitation and adsorption also fractionate Fe isotopically (Icopini et al., 2004; Skulan et al., 2002).

Despite all these processes that could fractionate Fe isotopically we observed that the bulk soil $\delta^{56}\text{Fe}$ values show very little variation throughout the diabase profile (Figure 3A; Table 2). Residual Fe in a regolith profile is expected to become isotopically heavy according to the following equation when isotopically light Fe is preferentially removed (Thompson et al., 2007):

$$d^{56}\text{Fe}_w = (d^{56}\text{Fe}_o + 10^3)f^{a-1} - 10^3 \quad (4)$$

Here $\delta^{56}\text{Fe}_0$ is the isotopic composition of the starting material ($-0.01 \pm 0.05\text{‰}$ for the diabase), f is the fraction of Fe remaining in the profile (equal to $\tau_{\text{Fe,Zr}}+1$), and α is the isotopic fractionation factor between aqueous and solid species.

Given that up to 80% of the Fe is lost from the most weathered horizons of the regolith profile (Table 2), the lack of $\delta^{56}\text{Fe}$ enrichment seems surprising. For example, if we assume that $10^3 \ln \alpha (\approx \delta^{56}\text{Fe}_{\text{aq}} - \delta^{56}\text{Fe}_{\text{solid}}) = \sim -0.3\text{‰}$ (the isotopic difference between the SRO phase and the bedrock composition at this site) and insert this value into Equation 3, an 80% Fe loss would result in residual regolith that is $+0.47\text{‰}$ heavier than the underlying bedrock. A lack of isotopic enrichment in more weathered samples (toward the surface) is therefore consistent with Fe loss occurring with minimal fractionation. As an example, colloidal transport of Fe-bearing phases such as smectite (with adsorbed Fe oxides) in the upper meter of the profile would not be expected to fractionate Fe. These colloids may either be translocated to other parts of the profile or may be lost from the soil profile altogether.

In contrast to bulk Fe, the HCl-extracted portion of the Fe in each sample is isotopically light. This fraction makes up no more than 10% of the total and is only 0.3‰ lighter than the bedrock value. The presence of a minor SRO phase therefore does not change the isotopic composition of the bulk Fe by more than 0.03‰ . Lack of variation in isotopic signature of total Fe in soils has been documented before, even in deeply weathered profiles. For example, in their analysis of Cameroon laterites, Poitrasson et al. (2008) observed minimal fractionation of bulk Fe, with $\delta^{56}\text{Fe}$ variations of $<0.2\text{‰}$ over a 36-m drill core that penetrated parent granodiorite, saprolite and Fe-rich horizons. This was despite the fact that up to 60% of the Fe had been lost from some of the horizons.

4.3. Identification of clay-sized fraction

Based upon XRD analysis of bulk samples by Hausrath et al. (2011), kaolinite and smectite both occur throughout the diabase profile. XRD diffractograms of clay-sized material from the regolith core indicate the following secondary weathering products: 1) a $14 \text{ \AA}$ phyllosilicate clay, 2) $7 \text{ \AA}$

kaolinite/halloysite and 3) quartz. Greater intensities of quartz toward the surface of the profile likely document eolian deposition at this site. In their study of a North Carolina diabase, Oh and Richter (2005) suggested that elevated Zr concentrations toward the surface of the profile may also be the result of eolian deposition. A similar elevation in Zr is noted in the upper 50 cm of the diabase profile as well (Hausrath et al., 2011). However, we argue that elevated Zr toward the surface at this site is mostly the result of weathering rather than eolian deposition. While the XRD quartz peak rapidly attenuates from 8 to 30 cm (Figure 4), Zr concentrations in the upper 50 cm are relatively constant (Hausrath et al., 2011).

In contrast to quartz, the intensity of the 14 Å peak in the clay-sized fraction does not change notably from 340 cm to 8 cm (Figure 4), indicating that this phyllosilicate phase forms at the bedrock-regolith interface and is present throughout the profile. XRD peaks corresponding to halloysite/kaolinite also indicate a 7 Å d-spacing that does not shift notably throughout the profile (Figure 4). Halloysite, identified throughout the profile with TEM, has a 1:1 Al:Si ratio and exhibits a wide variety of different morphologies, including tubular and spherical forms (Tazaki, 2005). Electron microscope images from other sites indicate that halloysite may form directly from plagioclase (Jeong et al., 2000; Papoulis et al., 2004). Other work has indicated an intimate association between halloysite and microorganisms (Minyard et al., 2011; Tazaki, 2005). The latter study is perhaps of particular interest here because Minyard et al. (2011) documented the formation of halloysite in the zone of Fe oxidation at the base of saprolite on the quartz granodiorite discussed previously.

Thermodynamic considerations predict that halloysite will convert into kaolinite with aging according to the following sequence observed in soils via electron microscopy: spherical halloysite → tubular halloysite → interconnected tubular halloysite → platy halloysite → newly formed kaolinite (Papoulis et al., 2004). In an investigation of regolith from the Piedmont of Virginia, Pavich et al. (1989) noted that halloysite, which was often present toward the bottom of the soil profile, tended to recrystallize to kaolinite toward the surface. This finding was true for regolith overlying metapelite, metagraywacke and granite. In contrast, we found morphological evidence of halloysite throughout the entire profile at

the diabase site, with no obvious transition to kaolinite toward the surface. This lack of transformation is not likely the result of differences in mean annual precipitation (104 cm/y versus 114 cm/y, respectively). A better explanation may be the lower temperature (10-12°C versus 12-14°C) in Pennsylvania compared to Virginia (Daly, 1994) and the higher curvature of the hillslope in PA compared to VA. This higher curvature may result in faster erosion in PA. Boulders seen at the surface of the PA site (but not in VA) further suggest that unweathered material in the Pennsylvania diabase is not reaching maturity.

4.4. Pore-water chemistry

Of all measurements, pore-water silica concentrations showed the most significant changes with depth (Figure 6C). Only a very weak correlation was observed between dissolved silica concentrations and DOC in the profile ($R^2=0.07$, $p<0.05$). In contrast, a very modest inverse correlation was noted between dissolved silica and pH ($R^2=0.27$, $p<0.001$), with higher silica concentrations at greater depth where the average pH was lower.

The soil pore-water pH as measured in the field increased from ~5.6 at 205 cm to ~6.3 toward the surface (Table 3; Figure 6A). This finding contrasts with soil slurry pH measurements showing lower pH near the surface (Hausrath et al., 2011). Lower pH toward the surface is generally expected given higher levels of organic matter and the presence of low-pH rainwater near the surface. Silicate weathering in the deep regolith is also expected to increase the pH.

We attribute decreases in pore-water pH with depth to the corresponding increases in the concentrations of soil gas carbon dioxide (Figure 6B). In these soils, the BC horizon may act as a restrictive barrier that limits upward diffusive loss of carbon dioxide. In many localities that have such a layer, low-pH, CO₂-charged fluids can accumulate at depth (Richter and Markewitz, 1995; Schulz et al., 2011). Low hydraulic conductivities at the Bt/BC interface have been attributed elsewhere to a lack of continuous pores at this depth due to fewer root channels and burrows, as well as thick cutans of translocated clay from the overlying soil (Buol and Weed, 1991). Because carbon dioxide will likely outgas with soil slurry measurements, pore-water and soil pH may often show very different trends.

Although there is a great deal of variation, average DOC and nitrate concentrations decrease with depth in the profile (Figures 6D and 6E; Table 3). Elevated nitrate concentrations at this site (of up to 30 mg/L) may be the result in part of anthropogenic nitrogen, which is high in the northeastern United States (Hedin et al., 1995). A decrease in DOC levels with depth is commonly observed due to precipitation, adsorption and decomposition of organic matter during downward migration of meteoric fluids (Dijkstra and Fitzhugh, 2003). However, maximum DOC concentrations are higher at this site (reaching values of 190 mg/L) than typically observed (1-50 mg/L) in many soil pore waters (Andrews et al., 2011 and references within) (Figure A.3).

Consistent with other studies (Lorieri and Elsenbeer, 1997; Tolpeshta and Sokolova, 2009), concentrations of pore-water Al, Fe and Mn roughly appear to decrease with depth in the diabase profile. However, the highest concentrations were found not in the surface samples but at the 60-cm depth, where Al and Fe concentrations of up to 1.2 mg/L were observed during different seasons (Table A.2). In contrast, the dissolved Al and Fe concentrations at depths below 60 cm were always ≤ 0.1 mg/L, while concentrations at the 16-cm depth never exceeded 0.26 mg/L (Table A.2; Figures 6F and 6G). Lysimeter pore-water samples collected from the 60-cm depth also had a distinct yellow color unlike that from any other sample depth. Although this color could be the result of colloidal material, elevated DOC concentrations at this depth suggest the presence of organic matter that may be complexing these metals. Elevated concentrations of DOC and metals at 60 cm may be the result of preferential flow along the Bt/BC horizon interface, likely a zone of low permeability (Buol and Weed, 1991). Elevated DOC and metals concentrations near certain horizon boundaries have been observed elsewhere in soils in PA (Andrews et al., 2011).

Within pore-water samples, DOC was more highly correlated with Fe and K ($R^2=0.60$, $p<0.001$ and $R^2=0.66$, $p<0.001$, respectively) than with Al and Na ($R^2=0.35$, $p<0.001$ and $R^2=0.24$, $p<0.001$, respectively). In contrast to Al, Fe, K and Na, no significant correlation was found between DOC and Mg ($p=0.46$). Although the mobilization of Al by DOC has been well documented within pore waters in soils

(Dijkstra and Fitzhugh, 2003; Tolpeshta and Sokolova, 2009), the correlation between DOC and Al is weaker at this site than for Fe. Nonetheless, these results document the important role of organic ligand complexation in the mobilization of dissolved Al and Fe in the upper part of the diabase profile.

4.5. Calculating diabase dissolution rates from solute chemistry

To understand the weathering system, we compared solid- and solute-based weathering rates in the upper two meters of the diabase profile from which pore waters were sampled. In theory, steady-state conditions in which the bedrock has attained a constant thickness over time would result in similar values for both of these rates (White et al., 2002). This would be of particular interest for the diabase study here because such a steady state would be consistent with a constant thickness of the diabase over time, which would in turn lead to the conclusion that lithogenic weathering at depth due to spheroidal weathering was occurring at the same rate overall as biogenic weathering near the surface. The following equation was used to calculate the diabase weathering rate based upon pore-water gradients in the upper two meters of regolith (White et al., 2002):

$$R_{solute} = 1000 \frac{1}{S_{BET} \beta} \frac{q_h}{b_p} \quad (5)$$

Here, R_{solute} ($\text{mol m}^{-2} \text{s}^{-1}$) is the surface-area normalized weathering rate based on solute chemistry, S_{BET} ($\text{m}^2 \text{m}^{-3}$) is the specific surface area, β (mol mol^{-1}) is the stoichiometric coefficient for the element in the dissolving mineral or rock, q_h is the flux density of water through the profile (m s^{-1}), and b_p (m L mol^{-1}) is the solute weathering gradient. For the bulk rock, the stoichiometric coefficient was assumed to be one Si atom per diabase formula unit ($\beta=1$). The approximate formula unit of the diabase is

$\text{Ca}_{0.23}\text{Na}_{0.08}\text{Mg}_{0.36}\text{Fe}_{0.11}\text{Si}_{1.00}\text{Al}_{0.57}\text{O}_{3.51}(\text{OH})_{0.27}$ (Hausrath et al., 2011). Based upon Si solute chemistry with depth, the average solute weathering gradient b_p ($\Delta z/\Delta c$) is equal to $\sim 1,600 \text{ m L mol}^{-1}$ (Figure A.5). The maximum flux density was set equal to the difference between average annual precipitation and average annual evapotranspiration (Brantley and White, 2009). Estimated mean annual precipitation

ranges from 100-125 cm/yr in central Pennsylvania, while evapotranspiration averages ~60 cm/yr (Sanford and Selnick, 2013); these values are consistent with a value of ~50 cm/yr (40-65 cm/yr) or ~1.6 x 10⁻⁸ m/s for the flux density. Based upon microscopic measurements of grain diameters and surface roughness, Hausrath et al. (2011) estimated plagioclase (~66% abundance) and pyroxene (~34% abundance) specific surface areas in the parent rock equal to 24,100 m²/m³ and 10,200 m²/m³, respectively. Based on an assumption of 66% plagioclase and 34% pyroxene, we calculate a bulk rock surface area (S_{BET}) of ~19,000 m²/m³.

The solute-based weathering rate calculated for the overall diabase based on dissolved Si in the upper two meters can then be compared with a similar calculation of the solid-state rate based on the upper two meters (White et al., 2002):

$$R_{solid} = 1000 \frac{r_w}{S_{BET} b} \frac{W}{b_s} \quad (6)$$

Here, R_{solid} (mol m⁻² s⁻¹) is the surface-area normalized weathering rate based on solid regolith chemistry. Given the long exposure time (Bazilevskaya et al., 2013), it was assumed that the rate of weathering advance (ω) was equivalent to the erosion rate (5 mm/ky or 1.6 * 10⁻¹³ m/s) (references within Hausrath et al., 2011). The average bulk density (ρ_w) of the profile was assumed to be 1 g/cm³ (Hausrath et al., 2011) and S_{BET} was set equal to the value discussed above (19,000 m²/m³). The Zr-normalized Si weathering gradient (b_s) was calculated to equal 0.4 m kg/mol⁻¹ in the upper two meters (Table A.4).

Using the above values, the dissolution rate of diabase based on pore-water chemistry (log rate = -12.3 (mol diabase m⁻² s⁻¹)) is only an order of magnitude faster than the rate calculated from solid chemistry in the upper two meters (log rate = -13.7 (mol diabase m⁻² s⁻¹)). Based on previous work in the central Appalachian Mountains (Potter et al., 2009; White et al., 2009), it is likely that the relatively similar values are evidence that the diabase profile is at steady state such that modern weathering rates based on solutes are equivalent to the time-integrated rates based on solid-phase chemistry. The

discrepancy between the solid- and solute-based calculations could easily be explained if the flux density in Equation 5 was overestimated, since lateral flow was not considered (Brantley and White, 2009). It is also possible that dissolution values calculated here from solute fluxes could be high for longer-term estimates because they fail to record lower weathering rates that may have existed under periglacial conditions (Price et al., 2005).

A constancy in rates of weathering advance over time is most likely to occur in systems where the erosion rate is also constant in time. This is because a perturbation in the erosion rate would thin or thicken a regolith profile and perturb porewater and soil gas chemistry, leading, in turn, to a change in the weathering advance rate. It is possible, therefore, that the diabase regolith at this location has maintained a roughly steady-state thickness for millennia despite a transition from the periglacial to the modern period. Intriguingly, such a constant thickness could only be maintained if the weathering advance at the top of the profile due to biogenic processes is equivalent to the rate at the bottom of the profile due to lithogenic processes. In that case, it is likely that the top of the profile is coupled to the bottom of the profile by pore water and soil gas chemistry.

5. Conclusions

The goal of this study was to use Fe isotopes, mineralogical observations, pore water measurements and gas chemistry to understand the formation of regolith on diabase, with a particular focus upon understanding processes related to Fe cycling that may be important in initiating regolith formation. Transmission electron microscopy (TEM) and EDS data for the clay-sized fraction of the regolith developed on diabase on a Pennsylvania ridge indicate a 14 Å phyllosilicate phase and halloysite/kaolinite as the main secondary weathering products throughout the profile.

Although the clay mineralogy is close to constant with depth, three zones of interest are highlighted within the regolith profile at this site. At the bottom (“lithogenic”) part of the profile, fractures in the diabase channelize fluid flow to initiate corestones in a zone dominated by rock + water + gas

reactions. Rindlets formed by fracturing around corestones are in turn converted into the lowermost regolith. In Zone 1, processes driving spheroidal weathering also produce a flux of isotopically light dissolved Fe(II) as pyroxene (or other minor ferrous minerals) dissolves. Due to the presence of O₂ in the soil atmosphere at depth, up to 90% of the Fe(II) is rapidly oxidized and precipitated as a SRO Fe phase. In accordance with other studies, pyrite oxidation also appears to be associated closely with the bedrock-regolith interface. While this zone lies at 360-400 cm depth and is not greatly affected by surface biota, it is possible or even likely that Fe-oxidizing bacteria may participate in the Fe cycling.

Zone 2, in the middle of the profile between the lower lithogenic and upper biogenic zones, is interpreted as a zone of crystallization in which SRO Fe precipitated at the bottom of the profile is ripening with time into more crystalline phases. This ripening leads to isotopically heavier signatures in SRO Fe as the lighter isotopes are preferentially mobilized by dissolution. Finally, zone 3 near the land surface is dominated by biotic processes and thus termed the biogenic zone. In that zone, SRO Fe concentrations and isotopically light Fe signatures are attributed to the effects of plant roots, which exude protons and organic acids capable of releasing isotopically light Fe into solution.

These observations are consistent with changes that occur in pore-water chemistry in the deeper B and C horizons. Average nitrate and dissolved organic carbon concentrations (DOC) in regolith pore fluids decrease with depth in the profile, documenting the influence of biota, especially in the biogenic upper layers. The pH values of pore-water samples decrease from the B to C horizons, presumably due to high concentrations of soil atmosphere carbon dioxide at depth which are trapped by the presence of a low-permeability layer at the Bt/BC interface. Pore-water cation concentrations (especially Fe) correlate with DOC throughout the year, as expected if dissolution of silicates and transport of Fe is dominated by organic complexation. Elevated concentrations of DOC, Fe and Al near the Bt/BC interface are consistent with preferential flowpaths, likely resulting from the lower hydraulic conductivity of the underlying BC horizon.

Similarities between this PA diabase and regolith on quartz diorite in Puerto Rico lead to the

inference that Fe oxidation may characterize initiation of weathering of bedrock in many ridge-top locations. Furthermore, Fe isotopes may document release of ferrous iron, oxidation, and precipitation at the bedrock-regolith interface. Specifically, precipitation of isotopically light Fe as SRO material is observed to accompany the Fe release and oxidation at the bedrock-regolith interface on both the diabase and the quartz diorite. Near the land surface, isotopically light SRO Fe is likewise observed in both the diabase and quartz diorite regolith profiles and is attributed to release of isotopically depleted iron due to biotic effects followed by precipitation. While we have labelled the upper and lower zones biogenic and lithogenic to emphasize the importance of biotic and abiotic processes near the surface and at depth respectively, it is likely that bacteria may participate in Fe release and oxidation, even at depth.

Weathering rates based on pore-water and solid-phase data are within an order of magnitude of one another, leading to the inference that today's rate of weathering is roughly coincident with the time-integrated rate in the past. The observation that solid- and water-chemistry data yield similar rates of weathering advance leads to the inference that the diabase regolith at this location has maintained a roughly steady-state thickness. This furthermore means that the rate of weathering advance at the top of the profile due to biogenic processes is equivalent to the rate at the bottom of the profile due to lithogenic processes. Coupling from the top to the bottom of the profile to maintain such a steady-state thickness could be maintained by pore-water chemistry and soil gas. Quantitative descriptions of weathering from parent material to the soil surface will only be possible if we can describe Fe oxidation reactions and soil gas chemistry at depth accurately.

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Tables:

Table 1: Description of diabase soil profile

Depth (m)	Horizon	
0-0.22	A	very dark grayish brown (10YR 3/2) silt loam with moderate, fine, subangular blocky structure; very friable; slightly sticky; common fine to medium roots throughout; clear lower boundary
0.22-0.60	Bt	strong brown (7.5YR 5/6) silty clay loam with moderate, medium, subangular blocky structure; friable; slightly sticky; common fine to medium roots throughout; few, distinct, discontinuous strong brown (7.5YR 5/6) clay films coating ped faces; clear lower boundary
0.60-0.90	BC	yellowish brown (10YR 5/8) sandy loam with weak, medium subangular blocky structure; very friable; slightly sticky; few fine roots; few yellowish red (5YR 5/8) clay films along ped faces; few, distinct black (N 2.5/) Mn coatings along ped faces and possibly tubular pores; clear lower boundary
0.9-1.60	C1	olive yellow (2.5Y 6/6) sandy loam, massive with zones of moderate, medium, angular blocky structure; laminated Fe concentrations (relict?); clear lower boundary
1.60-2.05	C2	strong brown (7.5YR 5/6) silt loam, common, distinct, black (N 2.5/) Mn coatings; auger boring terminated because of lystimer installment
2.05-2.30	C2	yellowish brown (10 YR 5/6) sandy loam
2.30-3.40	C3	olive yellow (2.5Y 6/6) sandy loam to loamy sand
3.40-3.65	C4	strong brown (7.5YR 5/6) silt loam; alternating layers of red (2.5YR 4/6) alternating with white (7.5YR 8/1) layers (rindlets?); red layers had possible pressure faces and black mottles along surfaces. This could be from augering.
3.65-3.95	C5	olive yellow (2.5Y 6/6) sandy loam to loamy sand
>3.95	R	bedrock

Table 3: Averaged pore-water data from fall of 2011 to the summer of 2013, with 1 standard deviation variation^a

depth (cm) ^b	pH	DOC (mg/L)	Al (mg/L)	Ca (mg/L)	Fe (mg/L)	K (mg/L)	Mg (mg/L)	Mn (mg/L)	Na (mg/L)	Si (mg/L)	nitrate (mg/L)	sulfate (mg/L)	chloride (mg/L)
16	6.3±0.3	32.9±25.2	0.1±0.1	12.3±3.0	0.0±0.0	2.9±3.1	2.8±0.6	0.0±0.1	1.2±1.7	9.7±2.3	9.9±8.1	5.3±2.3	3.1±2.6
63	6.3±0.2	39.0±45.0	0.2±0.2	7.5±3.2	0.2±0.3	7.2±7.0	3.6±1.4	0.0±0.1	4.2±3.0	12.8±1.5	6.6±8.6	10.7±4.8	3.7±4.3
95	6.1±0.4	11.3±13.4	0.0±0.0	10.1±1.9	0.0±0.0	1.4±0.6	2.3±0.4	0.0±0.0	1.2±0.4	12.2±1.3	1.8±2.9	6.2±1.4	2.1±1.7
126	6.0±0.2	9.9±11.9	0.0±0.0	9.1±0.7	0.0±0.0	0.2±0.1	5.7±0.4	0.0±0.0	3.6±0.3	26.3±1.8	2.2±2.0	12.1±2.9	2.1±1.4
205	5.6±0.3	3.5±2.2	0.0±0.0	9.5±0.4	0.0±0.0	0.2±0.1	5.5±0.2	0.0±0.0	3.2±0.1	30.5±1.8	2.1±0.4	11.0±0.8	1.5±0.3

a) All analytical methods discribed in text in greater detail.

b) Depths indicate depths at which lysimeters are installed.

Figures:

Figure 1. Study area. A: Map of eastern North America showing general location of profile in south-central Pennsylvania. B: Digital elevation model, with the yellow star indicating the sampling location. The turnpike roadcut from which the parent material was obtained is located ~2 kilometers to the north (See Hausrath et al. (2011) for location). The N-S trending linear ridge is the topographic expression of the Late Triassic diabase dike.

Figure 2. A) The percent of Fe present as Fe(II) in regolith with depth with the propagated error shown for depths of 81 cm, 379 cm and the bedrock sample assuming 5% error in total Fe concentrations with XRF analysis (Hausrath et al., 2011). Error bars at 81 cm and 379 cm are too small to see (Table 2). B) $\tau_{Zr,j}$ values with depth for total Fe (from Hausrath et al., 2011), Fe(II) and sulfur in the diabase regolith profile. The black stars in A) and B) indicate the composition of inferred bedrock material. The depth of the bedrock, which was obtained from the turnpike roadcut to the north, is arbitrarily plotted at 450 cm. Zones delineated in Figure 2B are explained in greater detail in Figure 7.

Figure 3. $\delta^{56}\text{Fe}$ values of A) bulk Fe and B) SRO (HCl-extracted) Fe as a function of depth in the regolith. Error bars show 2σ variation of replicate analyses. The lowermost point (star) indicates the isotopic composition of bulk Fe in bedrock taken from along the Pennsylvania Turnpike and is arbitrarily plotted at 450 cm. Horizontal lines in A) and B) indicate the depth of auger refusal, interpreted as the bedrock-regolith interface. Vertical line in A) indicates the isotopic composition of parent material. Circles in Figure 3B are data from Buss et al. (2010).

Figure 4. XRD diffractograms of the clay-sized fraction ($<2\ \mu\text{m}$) of the regolith at different depths. Peaks include: (1) a 14-Å clay (chlorite/vermiculite/smectite), (2) 7-Å kaolinite/halloysite and (3) quartz. Vertical gray lines indicate 7 and 14 Å peaks. Peaks are identified for only a few scans.

Figure 5. TEM images of the clay-sized fraction of the 340-350 cm diabase sample. Images include: A) a lower magnification image to demonstrate the heterogeneous morphology, B) a polycrystalline tube similar to reported halloysite morphology, C) an amorphous tube-like structure, and D) a rose-shaped morphology characteristic of halloysite. Tubular and rose-shaped halloysite were also observed in the clay-sized fraction of samples from 30 cm and 70 cm.

Figure 6. Average pore-water data with standard deviations plotted as a function of profile depth. A) pH, B) soil carbon dioxide (percent by volume) C) pore-water silica, D) pore-water dissolved organic carbon, E) pore-water nitrate, F) pore-water Al, G) pore-water Fe and H) pore-water chloride. Error bars indicate the 1σ variation over time for each depth.

Figure 7. Schematic of processes operating in the diabase profile. At the bottom of the profile, diabase corestones are transformed into onion-like rindlet zones. The rindlet zones in turn are converted into the lowermost regolith. Three major zones are identified in the figure. Zone 1 at the bottom of the profile is characterized by spheroidal weathering, which results in the flux of isotopically light Fe(II) into the lower portion of the profile with pyroxene weathering. Due to the well-oxidized nature of the profile, this Fe(II) is rapidly oxidized and precipitated as an SRO Fe phase. Zone 2 in the middle of the profile is interpreted as a zone of crystallization in which SRO Fe precipitated at the bottom of the profile is presumably ripening into more crystalline phases toward the middle of the profile. This ripening leads to isotopically heavier signatures as the lighter SRO phases are presumably lost during dissolution reactions. Finally,

855 isotopically light SRO Fe signatures at the surface are attributed to the effects of plant roots, which exude
856 both protons as well as organic acids. See discussion for further details.
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Figure 1.

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