How Oxidation and Dissolution in Diabase and Granite Control Porosity during Weathering

Weathering extends to shallower depths on diabase than granite ridgetops despite similar climate and geomorphological regimes of denudation in the Virginia (United States) Piedmont. Deeper weathering has been attributed to advective transport of solutes in granitic rock compared to diffusive transport in diabase. We use neutron scattering (NS) techniques to quantify the total and connected submillimeter porosity (nominal diameters between 1 nm and 10 μm) and specific surface area (SSA) during weathering. The internal surface of each unweathered rock is characterized as both a mass fractal and a surface fractal. The mass fractal describes the distribution of pores (~300 nm to ~5 μm) along grain boundaries and triple junctions. The surface fractal is interpreted as the distribution of smaller features (1–300 nm), that is, the bumps (or irregularities) at the grain–pore interface. The earliest porosity development in the granite is driven by microfracturing of biotite, which leads to the introduction of fluids that initiate dissolution of other silicates. Once plagioclase weathering begins, porosity increases significantly and the mass + surface fractal typical for unweathered granite transforms to a surface fractal as infiltration of fluids continues. In contrast, the mass + surface fractal does not transform to a surface fractal during weathering of the diabase, perhaps consistent with the interpretation that solute transport is dominated by diffusion in that rock. The difference in regolith thickness between granite and diabase is likely due to the different mechanisms of solute transport across the primary silicate reaction front.

Abbreviations: FIB, focused ion beam; NS, neutron scattering; RZ, reaction zone; SANS, small-angle neutron scattering; SAP, saprolite zone; SEM-EDS, scanning electron microscopy with energy dispersive spectrometer; SLD, scattering length density; SSA, specific surface area; USANS, ultra-small-angle neutron scattering; UWR, unweathered rock; WR, weathered rock; μ-CT, microcomputed X-ray tomography.

Weathering, the transformation of intact rock into soil through physical and chemical reactions, is a key process that affects the CO₂ cycle, soil formation, and nutrient uptake into ecosystems. Upon reaction with meteoric fluids, pristine parent rocks transform from relatively nonporous material to porous weathered material (soil and saprolite), which we term here regolith (Brantley and White, 2009; Buol and Weed, 1991; Pavich et al., 1989). The earliest weathering-related mineral-fluid interactions are thought to be largely controlled by the distribution of the connected porosity and the topography of the pore interface at the nanometer scale (Hochella and Banfield, 1995). When interconnected, these pores likely allow solute transport only by diffusion in relatively pristine, low-porosity crystalline rocks. For instance, in unweathered granite rocks with low porosity, microcracks and elongated voids can be the most important pathways of solute transport (Sausse et al., 2001). During weathering and rock disaggregation, solute
transport by diffusion eventually is outcompeted by transport by advection as fractures interconnect and larger micrometer-sized pores form from smaller pores. However, this transformation from a regime dominated by diffusion to one dominated by advective transport and the role of pore-scale reactions on rock weathering are not well understood (Navarre-Sitchler et al., 2013; Rossi and Graham, 2010; Nahon, 1991).

In our previous work, we investigated aspects of the relationship between mineral reaction and porosity in two crystalline rocks weathering in the same climate at similar erosion rates (Bazilevskaya et al., 2013; Brantley et al., 2014). These two rocks, a diabase and a granitic rock, had been previously cored and studied by workers in the 1990s (Pavich et al., 1989). Both rocks are dominated by plagioclase (58% Ca-rich feldspar in diabase; 52% Na-rich feldspar in granitic rock). Although the diabase contained the more fast-dissolving plagioclase composition (An$_{60}$), it was characterized by a much thinner weathering profile: the regolith was only about 1 m thick. In contrast, the granitic parent contained the more slow-dissolving plagioclase (An$_{06}$) but had developed a much deeper regolith (20 m). Bazilevskaya et al. (2013) suggested that oxidation of biotite occurred between the 22- and 20-m depth in the granite, causing fracturing of the rock that allowed advection at depth. The advection controlled the solute transport and resulted in formation of deep regolith; in turn, permeability in the deep regolith was maintained by the high concentration of quartz grains in the granitic rock. Similar fracturing was not observed in the diabase profile, and the lack of quartz further precluded maintenance of high permeability. Furthermore, by inspection of a compilation of regolith depths as a function of lithology, Bazilevskaya et al. (2013) concluded that regolith depth was commonly thicker on granitic material compared to diabase when observed at ridgetop locations in many locations worldwide. Brantley et al. (2014) explored this idea further and pointed out that the high ferrous Fe content of rocks such as diabase could deplete downward percolating fluids of O$_2$ before depletion of CO$_2$ when they weathered in ridgetop locations. In contrast, in felsic granites, CO$_2$ is likely to be depleted before O$_2$ due to the high content of weatherable base cations but low content of Fe(II). Those authors inferred that the relative depths of the oxidation vs. the silicate dissolution fronts in a crystalline rock may predict whether oxidation-related fracturing occurs during weathering.

Building on our previous work on the Virginia rocks described above, this study focuses specifically on nano- to micrometer-scale changes in the pore network that occur during weathering reactions in the diabase and granite. We use small-angle neutron scattering (SANS) and ultra-small-angle neutron scattering (USANS) to quantify porosity and surface features ranging in size from 1 nm to 5 μm in crystalline and sedimentary rocks (Wenk, 2012; Anovitz et al., 2009; Radlinski, 2006). We complement the neutron data with microcomputed X-ray tomography (μ-CT) to quantify porosity at the 3 to 500 μm scale, defined in this work as mesoporosity. Microcomputed tomography provides the opportunity to observe and quantify sample porosity without sample destruction. In addition, we use energy dispersive X-ray scanning electron microscopy (SEM-EDS) to elucidate the mineralogy, chemical composition, and grain distribution, as well as the shape and grain contact morphology of the different mineral phases and pores.

**DESCRIPTION OF THE WEATHERING PROFILES**

The weathering profiles on granitic and diabase rocks that we study here have developed on hilltops in the Piedmont province in Fairfax County, VA (Fig. 1a) as described in previous publications (Bazilevskaya et al., 2013; Brantley et al., 2014; Pavich et al., 1989). To summarize, the Piedmont province is a rolling upland plain developed on diverse underlying metamorphic and igneous rocks. The province is characterized by minor relief, moderate elevation (90–200 m), and mature deciduous forest cover. In this region, the summers are generally warm and humid, and the winters are mild with mean average temperature equal to 10°C. Summer temperatures reach 38°C, and the minimum winter temperature can be lower than −20°C. The maximum rainfall intensity occurs in summer with average rainfall of 1040 mm yr$^{-1}$. The longest drought period generally occurs during fall. Most groundwater storage in the Piedmont is within the regolith (especially within the saprolite), but minor storage also occurs in joints and fractures in fresh rock (Pavich et al., 1989). The stable erosion rates have been estimated from cosmogenic isotopes, exposure time, and elevation to equal 4 to 8 m per 1 × 10$^{6}$ yr (Bacon et al., 2012; Price et al., 2008; Pavich et al., 1985). Residual weathering profiles have developed over the parent rocks. As a result, Alfisol soils, Kelly (fine, vermiculitic, mesic Aquic Hapludalfs) and Jackland (fine, smectitic, mesic Aquic Hapludalfs) series, are present on the granitic and diabase rocks, respectively.

We report analyses of cores of diabase that were taken from a ridge top (elevation ~91 m asl) adjacent to a diabase quarry in the Triassic Culpepper basin in the western Piedmont province by Pavich and colleagues (Pavich et al., 1989). Samples of the granitic rocks were collected in the highest upland (elevation ~135 m asl) immediately north of the Occoquan River as continuous cores from surface to unweathered rock. The granitic rock is a metamorphosed quartz monzonite (adamellite) (Seiders et al., 1975). The weathering profiles of both rocks grade upward from fresh bedrock to the soil surface (Pavich et al., 1989). The profiles include unweathered rock (UWR, i.e., bedrock), weathered rock (WR), overlying saprolite (SAP), and soil (referred to as SOIL in diagrams; Fig. 1b).

In the unweathered diabase, no alteration was visible except for Fe hydroxide stains along joint planes. The diabase consists of 54.0 v/v plagioclase feldspar (labradorite, An$_{60}$) and 36.2 v/v pyroxene with minor orthoclase, ilmenite, and magnetite (Bazilevskaya et al., 2013). The WR zone is comprised of intact diabase with slightly altered pyroxene and less altered plagioclase. In the SAP zone, that is, the soil Cr horizon, the saprolite consists of altered fragments (1–5 mm in diameter) of diabase, and the material is easily crushable by hand due to the
loss of mechanical strength and density, but with the structure still preserved. The clay fraction (<2 μm particle size) comprises 15 to 25% and up to 55% in SAP and SOIL zones, respectively. The major secondary clay mineral in the SAP zone is expandable smectite. Smectite alters to nonexpandable vermiculate higher in the SOIL zone.

The weathering profile of the granitic rock is 20× deeper than that of the diabase (Fig. 1b). The unweathered granitic parent rock is characterized by low to medium permeability, no Fe stains along joints and no weathering of feldspars. In the UWR zone, the unaltered granite consists of 40.5 v/v quartz, 32.0 v/v plagioclase (An60), 3.4 v/v muscovite, and 3.7 v/v biotite (Bazilevskaya et al., 2013). Fresh granitic rock (UWR) gradually transforms into hard and moderately WR and then to firm (but less dense and highly altered) SAP. The overlying weathered rock zone has medium to high permeability and exhibits alteration of feldspars and mafic minerals (Pavich et al., 1989). The granular granitic saprolite is composed of hard, resistant fragments of quartz 1 to 5 mm diam. and corresponds to a Cr-horizon in the soil profile. The original structure and texture are preserved in the SAP, but feldspar has significantly altered. The clay fraction comprises <10% in saprolite, <25% in the lower part of the soil zone, but reaches up to 45% in the upper 0.5 m of soil. Kaolinite is a dominant constituent, and muscovite is a minor constituent of the clay fraction in the saprolite shallower than the 14.9-m depth as reported previously by (Pavich et al., 1989).

**Mineral Reactions in Granite and Diabase Profiles**

In our previous publications (Bazilevskaya et al., 2013; Brantley et al., 2014), we studied mineral weathering reactions in terms of changes in bulk elemental concentrations using the mass transfer coefficient ($\tau_{ij}$) (see Fig. 2 caption for the equation). Since plagioclase was the most abundant and easily weathered mineral in the granite while plagioclase and pyroxene together were the most abundant and easily weathered minerals in the diabase, we used Na as a proxy for plagioclase and Mg and Ca as a proxy for pyroxene to follow the corresponding mineral dissolution reactions in weathering profiles (Fig. 2) (note that in diabase Ca was contained both in plagioclase [An60] and pyroxene).

![Fig. 1. (a) Physiographic divisions of Fairfax County, VA (after Pavich et al., 1989) and diabase (F18, F19) and granite (F11) sites location. (b) Diabase and granite weathering profiles developed on diabase and granite. Asterisk denotes samples chosen for neutron scattering measurements. Zone notation: SAP, saprolite; SOIL, soil; UWR, unweathered rock; WR, weathered rock.](image)

Fig. 2. Mass transfer coefficient ($\tau_{ij}$) plots for Na (circles), FeO (triangles), FeOoxidized (spheres), and strain (blue triangles) for (a) diabase, and (b) granite profiles. Data from Pavich et al., 1989 and this study. The $\tau_{ij}$ values were calculated using the following equation (Brimhall and Dietrich, 1987; Anderson et al., 2002):

$$\tau_{ij} = \frac{C_{wj}}{C_{ip}} \times \frac{C_{ip}}{C_{ij}} - 1$$

Here $C_{wj}$ and $C_{ip}$ are concentrations of mobile element $j$ in weathered zone (subscript $w$) and parent (p) rock, respectively, and $C_{ip}$ and $C_{ij}$ are concentrations of immobile element $i$ in weathered zone and parent rock, respectively. Negative $\tau_{ij}$ values indicate depletion of $j$ in regolith with respect to $j$ in the parent, for example, $t = -1$ indicates that element contained in parent rock was completely depleted during the weathering process. Values of zero indicate no change of the element of interest with respect to the parent, and $\tau_{ij} > 0$ indicate enrichment of the element of interest $j$ in weathered material compared to parent concentration. Parent rock composition for both diabase and granite was taken as an average composition of the two deepest rocks in each profile where no changes in chemistry or bulk density were observed. Figure is reproduced from Bazilevskaya et al., 2013; Brantley et al., 2014). SAP, saprolite; SOIL, soil; UWR, unweathered rock; WR, weathered rock.
From our previous findings, we concluded that Na comprised a fully developed weathering profile, that is, the profile varied from parent concentration at depth (t = 0) to completely depleted (t = −1) at the surface in both the granite and diabase (Fig. 2). Sodium depletion occurred in the SAP zone alone in the diabase, while about 50% of the Na was lost in the WR zone of the granite profile. In the diabase, Ca and Mg also showed depletion (like Na) in the SAP zone. All three elements were completely (100%) depleted at the land surface. Thus, according to the bulk chemistry, plagioclase began to dissolve in the WR zone in the granite, but pyroxene + plagioclase both began to dissolve higher in the profile (in the SAP zone) in the diabase.

The fraction of Fe(II) depleted from the profiles, \( \tau_{\text{FeO}} \), was calculated using bulk FeO concentrations. Although some of the ferrous Fe was leached from the weathering profile, Fe was also reprecipitated as Fe(III) (oxy)hydroxides. For each profile, we compared the initial concentration of Fe(II) and Fe(III) in the parent to the concentration after weathering to calculate how much of the ferrous Fe was oxidized and retained in the rock, referred to here as “FeO oxidized,” that is, FeO oxidized = \( C_{\text{FeO,p,w}} - C_{\text{FeO,p,oxidized}} \). To assess this component, we calculated a mass transfer coefficient (found in Eq. [1]), to express the fraction of Fe(II) in the parent material that accumulated as an Fe(III) oxide in regolith (Fig. 2).

\[
\tau_{\text{FeO}} = \frac{2 \left( C_{\text{FeO,p,w}} - C_{\text{FeO,p,oxidized}} \right) C_{\text{Ti,p}}}{C_{\text{FeO,p,w}} C_{\text{Ti,w}}} \quad [1]
\]

Here, subscripts p and w denote concentrations in parent and weathered material, respectively; all concentrations are expressed in mol kg\(^{-1}\).

Iron behavior during weathering reflected the presence of \( \text{O}_2 \) in the soil atmosphere and the depths at which oxidation reactions took place. In granite, much of the ferrous Fe was contained in biotite (~3.7 v/v), whereas in the diabase the ferrous Fe was present in pyroxene (36.2%). In the granite, depletion of FeO took place to a very small extent in the WR zone as plagioclase and pyroxene dissolution, and most of this FeO depletion near the land surface was accompanied by Fe(III) precipitation. Deeper in the system, FeO depletion without Fe(III) precipitation took place to a very small extent in the WR just below the interface with the SAP. Loss of ferrous Fe at depth was attributed to weathering in a low-\( \text{O}_2 \) atmosphere. Apparently, just above the WR-SAP interface, \( \text{O}_2 \) was present, but it became depleted in the WR (Fig. 2).

In this paper, we examine in greater detail how porosity and mineral surface properties have developed in these rocks using new neutron scattering analysis and complementary imaging methods. We hypothesize that nanoporosity plays a vital role in weathering reactions in diabase and granite profiles.

**METHODS**

**Chemical Characterization of Weathering Profiles Major Element Concentrations**

Bulk chemical composition for major elements for the samples used for neutron scattering were analyzed by inductively coupled plasma optical emission spectrometer (ICP–OES) at a commercial geochemical laboratory (SGS Canada Inc., method ICP95A). Additional chemical data were also reported previously (Pavich et al., 1989).

**Sulfur Concentrations**

Total sulfur concentrations in the granitic and diabase samples were measured by LECO Sulfur Analyzer Coulometer at the Material Characterization Laboratory, Penn State. This instrument measures the amount of 0.1 M KIO\(_3\) required to titrate the \( \text{SO}_2 \) formed as a result of combustion of each sulfur-containing sample. To complete the analysis, ~500 mg of powdered sample were added along with granular Sn metal and Fe chips to ceramic crucibles and capped with ceramic lids following LECO protocol. Tin and Fe beads, supplied by the LECO Corporation, were added to the samples to aid combustion (Jones and Isaac, 1972). The amount of KIO\(_3\) is proportional to the \( \text{SO}_2 \) evolved from the sample which, in turn, is proportional to the %S in the sample:

\[
\%S = \frac{C_{\text{KIO}_3} V_{\text{KIO}_3}}{0.001 M_{\text{KIO}_3} m_{\text{sample}}} \times 100\% \quad [2]
\]

Here, \( C_{\text{KIO}_3} \) represents the concentration of potassium iodide in the titrant (g L\(^{-1}\)), \( V_{\text{KIO}_3} \) is the volume of potassium iodide added to restore the color (L), \( M_{\text{KIO}_3} \) and \( M_s \) are the molecular weights of KIO\(_3\) and S, respectively, and \( m_{\text{sample}} \) is the mass of the sample (mg). In this equation, 3 equals the number of moles of \( \text{SO}_2 \) needed to neutralize1 mole of KIO\(_3\), and 0.001 is the conversion factor from grams to milligrams. A sulfur standard provided by LECO (a 1000-mg metal ring that contains 0.0288% ± 0.001 S) was also analyzed. Blank crucibles were analyzed at the beginning and end of each run. A total of 17 standards were measured and the average over multiple days was (0.0254 ± 0.0025)%. The accuracy for this standard was thus ±0.0034% (= 0.0288–0.0254) absolute error and 11.8% relative error (equal to 0.0034/0.0288). For the samples with no organic matter (UWR and WR and deep SAP), it was assumed that total S is equal to inorganic sulfur in sulfides.

**Carbonate Concentration**

Carbonates (inorganic carbon) were measured using a modified version of a published procedure (White et al., 1999). Samples measuring 1 to 2 g were ground to pass a 100-mesh...
(≤150 µm) sieved, placed in serum bottles, and sealed. Next, air was evacuated from the bottles by flushing high purity N2 gas, then 5 mL of 1 N HCl were injected through the rubber stopper using a needle syringe. After HCl reacted with carbonates in the sample, CO2 was released into the bottle headspace according to the reaction, CaCO3 + H+ = Ca2+ + CO2 + H2O. After 24 h of shaking to ensure the reaction was complete, samples were analyzed by LI-COR CO2–H2O Analyzer (LI-7000) in the Biogeochemistry Laboratory, Department of Crop and Soil Sciences, Penn State. Headspace concentrations of CO2 were converted to mg C kg−1 using atmospheric pressure, air temperature, jar volume, subsample volume, and sample weight. A series of blank samples (air) were also measured, and the average blank value of C was subtracted from the measured C concentrations to obtain carbonate content in rock samples. The calibration curve was created by injecting known amounts of CO2 into the instrument from gas tanks with either 970 or 10,010 mL L−1 CO2. We used calibration curve standards to estimate accuracy and relative error. Each of the four standards (2.5, 5, 10, and 25 mL L−1) was used calibration curve standards to estimate accuracy and relative error. Each of the four standards (2.5, 5, 10, and 25 mL L−1) was measured four times over multiple days to obtain 2.30 ± 0.18, 9.01 ± 0.46, and 25.53 ± 2.075 mL L−1. Thus, the average relative error was 5.8%.

**Porosity Characterization**

**Neutron Scattering**

We use SANS and USANS to statistically characterize structural features at nanometer to micrometer length scales. The coherent scattering originates primarily from pores within the rock matrix, due to the large scattering length density contrast between minerals and voids (Anovitz et al., 2009; Cole et al., 2006; Radlinski, 2006). The scattering intensity is measured as a function of scattering angle, θ, which is related to the momentum transfer or scattering vector Q through the equation $Q = \frac{4\pi}{\lambda} \sin(\theta/2)$. The normalized scattering intensity, $I(Q)$, is proportional to the number and volume of scatterers, the scattering contrast, and a function describing the shape and size distribution of scatterers. The nanopore systems found in rocks are commonly comprised of irregularly shaped pores with a broad distribution of pore sizes and varying degrees of connectivity. A typical scattering plot is shown in Fig. 3 where $I(Q)$ is the intensity of scattered neutrons as a function of the scattering vector Q. The value of Q corresponds to the inverse of the size of the scatterer, d, that is, $d \sim 1/Q$ for crystalline structures, which are typical for rocks. The scattering curve shows higher scattering intensity from the weathered compared to the pristine rock at all values of Q. This is consistent with a larger pore-size distribution in the altered, more porous material (Fig. 3). The creation of porosity and rock-pore interfaces during weathering can be quantified using NS techniques, and fractal concepts have proven to be particularly useful for the description of rock pore systems.

Rock samples for neutron scattering were prepared as double-polished thin sections mounted on a quartz slide and placed on a cadmium plate (which has high neutron absorption) with an aperture of diameter 15.9 mm to define the neutron beam incident onto a circular section of the rock. Small-angle neutron scattering measurements were conducted on the NG7 pin-hole instrument at NCNR (Glinka et al., 1998), covering the entire accessible range of $3 \times 10^{-5}$ Å−1 < Q < 0.4 Å−1 using a neutron wavelength of 8.09 Å. Complementary USANS data covering the range of $5 \times 10^{-5}$ Å−1 < Q < $2 \times 10^{-3}$ Å−1 were obtained using the BT5 double-crystal instrument (Barker et al., 2005) at NCNR using a wavelength of 2.38 Å. The raw data were corrected for background, scattering from an empty slide, detector efficiency, and sample transmission and normalized to absolute intensities using the NCNR software (Kline, 2006). The USANS data were in addition corrected for the slit geometry using the NCNR routines.

Intensities in the higher Q range measured by SANS correspond to scatterer diameters d in the range ~1 nm < d < 200 nm (Fig. 3), and the lower Q data measured by USANS corresponds to scatterer diameters in the range up to 10 µm. Combining data from SANS and USANS, the features measured by neutron scattering range in size from 1 nm to 5 µm. Pores in this size range are referred to here as nanopores.

Porosity was calculated assuming the random two-phase approximation of minerals and pores from the scattering invariant Z.

$$Q_{\text{max}} \int_{0}^{\infty} I(Q)Q^{2}dQ = Z = 2\pi\chi(D\rho)^{2} \times \phi \times (1-\phi) \quad [3]$$

![Fig. 3. A characteristic plot of the neutron scattering intensity I(Q) vs. scattering vector Q (for unweathered [G4] and weathered [G3] granite). High Q values are obtained by small-angle neutron scattering (SANS) and low Q values are obtained by ultra-small-angle neutron scattering (USANS). The dimension of objects (pore diameter, nm) that contribute most to the scattering for any given Q-value equals 2.5/Q (Radlinski, 2006). The sample that was weathered shows more scattering. Note that the difference in scattering between unweathered granite (G4) and weathered granite (G3) is prominent. Unweathered G4 shows a break in slope at Q ~ 2 × 10^{-3} Å^{-1} (~200 nm in pore size). The slope at low Q (<2 × 10^{-3} Å^{-1}) and high Q (>2 × 10^{-3} Å^{-1}) corresponds to mass fractal (m < 3) and surface fractal (m > 3), respectively. Note that the weathered rock does not show a break in the slope and is a surface fractal.](image-url)
where $\Delta \rho$ is the coherent neutron scattering length density contrast between the rock matrix and the pores (voids) and $\phi$ is the volume fraction of pores in the rock.

To determine the neutron coherent scattering length density (SLD) of the rock matrix, the chemical composition (bulk chemistry data) and pycnometric density for each sample were measured. These generalized chemical formulas and grain densities were then used to calculate SLDS of the rock phases using the NIST SLD calculator (www.ncnr.nist.gov/resources/sldcalc.html, accessed 13 Oct. 2014).

To determine the fraction of interconnected nanopores, the samples were immersed for 3 d in a suitable $^2$H$_2$O–H$_2$O mixture that was mixed to be contrast-matched with the sample grains. Specifically, a $^2$H$_2$O mass fraction of 0.67 yielded a liquid with a similar SLD as the mineral matrix ($4 \times 10^{-6}$Å$^{-2}$). To ensure that the sample remained water-saturated during the scattering, it was placed between two glass plates and sealed with a rubber gasket, while immersed in a small amount of contrast-matched water. Saturation of the connected pore fraction with contrast-matched water via capillary forces leads to zero scattering contrast between the nanopores and the rock; therefore, only unconnected pores scatter in contrast-matched samples. The difference in scattering intensities between dry and wet samples was determined and attributed to scattering from connected pores.

The PRINSAS software (Hinde, 2004) was used to calculate SSA of the mineral-pore interface. The distribution of pore sizes and shapes is approximated using the polydisperse hard sphere model. The SSA is calculated from the pore size distribution as the sum of surface areas of all pores with radius larger than $r$, $S\left( r \right)$, divided by the sample volume, $V$ (Radlinski, 2006):

$$SSA = \frac{S\left( r \right)}{V} = \frac{n_s}{r} \int_0^{r_{max}} A_s f\left( r \right) dr$$

[4]

where $n_s$ is the average number of pores per unit volume, and $A_s$ equals $4\pi r^2$ minus the pore area. This latter expression is based on the representation of the independent spherical pores with distribution $f\left( r \right)$ where $r$ is pore radius.

Small-angle neutron scattering/USANS measurements were completed on four diabase samples derived from two cores from boreholes drilled ~25 km apart (Pavich et al., 1989): D1 (sample from core F18 at the interface between WR and SAP), D2 (from WR in F18), D3 (at the interface between WR and UWR in F19), and D4 (from UWR in core F19) (Fig. 1b, left).

Four granite samples were selected from the F11 core: G1 (from SAP), G2 (from the interface of SAP and WR), G3 (at the interface between WR and UWR), and G4 (from UWR) (Fig. 1b, right). Samples G1 and G2 are powdery saprolites with a quartz-rich matrix (Pavich et al., 1989). The primary structure was less preserved in G1 than G2. Sample G3 is a firm rock in which original structure and textures are preserved. Sample G4 is a relatively fresh rock with minor Fe staining on joint planes.

Microcomputed Tomography

The entire set of samples used for neutron scattering plus two additional samples from the diabase SAP zone were characterized with $\mu$-CT. Small bedrock chips (~1 mm diam., 4–5 mm in length) were measured by synchrotron X-ray-based 3D $\mu$-CT (Beamline 8.3.2 at the Advanced Light Source at Lawrence Berkeley National Laboratory) to obtain images with a 0.8-μm pixel size. Samples were mounted on a specifically designed sample holder and illuminated by X-rays of 25 keV. These X-rays penetrate the sample and are attenuated as a function of density of the material with lower density material (pores) attenuating X-rays to a lesser degree. This method is a nondestructive technique to image and measure sample porosity for pores of diameter >3 μm. Filtered back-projection tomographic reconstruction was performed using Octopus software (Dierick et al., 2004). Further image analysis—including anisotropic diffusion filtering, threshold-based segmentation, connected component analysis, and skeleton analysis—were performed using Avizo Fire software (Peth, 2010). Porosity was quantified for several subsamples, each with an average volume of 0.08 ± 0.03 mm$^3$. Porosity from $\mu$-CT is referred to here as mesoporosity.

Spectroscopy

The size and composition of primary and secondary minerals and pore shape and distribution were measured by FEI Quanta 200 Environmental SEM coupled with EDS using a backscatter electron detector at the Materials Characterization Laboratory, Penn State. Compositions of major minerals were detected with repetitive measurements on several grains of the same mineral. Complementary transmission electron microscopy was completed on a JEOL 2010F TEM to study nanopores in the diabase. Samples were prepared for TEM using a focused ion beam (FIB) to produce thin (100 nm) foils of diabase. Foils were prepared on a Hitachi S-3500N FIB-secondary electron microscope at the Materials Research Institute, Penn State, and observed under TEM.

RESULTS

Chemistry of Diabase and Granite

The bulk chemical composition for granite and diabase samples selected for NS measurements are shown in Table 1. The averaged composition obtained from the two deepest samples was defined as a parent rock composition for both diabase and granite profiles and was used to plot t vs. depth (Fig. 2). As discussed in the next section, the weathered rock was always a stronger scatterer of neutrons than the parent rock because of its higher porosity (Fig. 3).

Carbonates and S concentrations are shown in Table 2. Although the data points are limited in number, carbonates were enriched in the diabase WR at the location where pyroxene begins to dissolve (see later discussion of Fig. 5), and in the SAP where plagioclase begins to dissolve (compare Na data in Fig. 2); similarly, carbonate was enriched in the granite WR zone in the plagioclase reaction front (compare Fig. 4 and Fig. 2). Such car-
bonate enrichment could contribute to some extent to the more than 4 to 5 \( \times \) increase of the LOI in WR and SAP compared to the granite UWR rock (Tables 1 and 2).

In diabase, the total S in the 13 WR and SAP samples averaged 0.0038 ± 0.0035%. In contrast, the four UWR samples averaged 0.0078 ± 0.0020. Although the very limited number of S measurements for the granite performed in this study yielded highly variable concentrations, the highest S concentrations were also measured in the UWR and WR (Fig. 4).

### Nanoporosity in Diabase

#### Anisotropy of Scattering Patterns

Figure 5a shows the two-dimensional patterns of scattered neutron intensity that were observed on the area detector for the diabase protolith (UWR) and weathered samples. The colors range from black (low intensity of scattered neutrons) to white (high intensity). Note that iso-intensity contours are radially isotropic only for UWR: scattering is equally intense in all directions for that sample. This is consistent with scattering from randomly-oriented scatterers. In contrast, all WR diabase samples show anisotropic scattering patterns. Anisotropy indicates presence of anisotropically-shaped pores with preferred orientation. In samples from the same depths observed under CT, TEM, and SEM, we observed elongated pores (~20–100 nm \( \times \) ~500–900 nm) distributed along boundaries between exsolution lamellae in pyroxene grains (Fig. 5b).

### Nanoporosity and Specific Surface Area

Although samples from UWR and WR diabase located within only 1 m of each other showed pronounced differences

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### Table 1. Bulk chemical composition of diabase and granite samples used in neutron scattering measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth</th>
<th>( \text{Al}_2\text{O}_3 )</th>
<th>( \text{CaO} )</th>
<th>( \text{Cr}_2\text{O}_3 )</th>
<th>( \text{Fe}_2\text{O}_3(\text{t}) )</th>
<th>( \text{K}_2\text{O} )</th>
<th>( \text{MgO} )</th>
<th>( \text{MnO} )</th>
<th>( \text{Na}_2\text{O} )</th>
<th>( \text{P}_2\text{O}_5 )</th>
<th>( \text{SiO}_2 )</th>
<th>( \text{TiO}_2 )</th>
<th>( \text{Zr} )</th>
<th>( \text{LOI} )</th>
<th>ml L(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diabase†</td>
<td></td>
<td>( % )</td>
<td>( % )</td>
<td>( % )</td>
<td>( % )</td>
<td>( % )</td>
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<td>( % )</td>
<td>( % )</td>
<td>( % )</td>
<td>( % )</td>
<td>( % )</td>
</tr>
<tr>
<td>D1 (WR)</td>
<td>1.03</td>
<td>13.8</td>
<td>10.8</td>
<td>0.03</td>
<td>11.3</td>
<td>0.55</td>
<td>7.19</td>
<td>0.17</td>
<td>2.1</td>
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<td>49.1</td>
<td>1.11</td>
<td>80</td>
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<tr>
<td>D2 (WR)</td>
<td>1.8</td>
<td>15.7</td>
<td>11.1</td>
<td>0.03</td>
<td>10.4</td>
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<td>6.68</td>
<td>0.16</td>
<td>2.6</td>
<td>0.12</td>
<td>52</td>
<td>0.99</td>
<td>90</td>
<td>0.25</td>
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</tr>
<tr>
<td>D3 (WR)</td>
<td>2</td>
<td>14.7</td>
<td>11.1</td>
<td>0.03</td>
<td>11.3</td>
<td>0.6</td>
<td>7.09</td>
<td>0.18</td>
<td>2.4</td>
<td>0.13</td>
<td>51.6</td>
<td>1.0</td>
<td>90</td>
<td>&lt;0.01</td>
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<tr>
<td>D4 (UWR)</td>
<td>2.75</td>
<td>14.3</td>
<td>11.2</td>
<td>0.03</td>
<td>12</td>
<td>0.54</td>
<td>7.25</td>
<td>0.19</td>
<td>2.3</td>
<td>0.2</td>
<td>50.8</td>
<td>1.13</td>
<td>90</td>
<td>0.90</td>
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<tr>
<td>G1 (SAP)</td>
<td>6.8</td>
<td>16.5</td>
<td>0.04</td>
<td>0.01</td>
<td>2.34</td>
<td>2.84</td>
<td>0.49</td>
<td>0.03</td>
<td>&lt;0.1</td>
<td>&lt;0.01</td>
<td>69.7</td>
<td>0.3</td>
<td>160</td>
<td>5.89</td>
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</tr>
<tr>
<td>G2 (SAP)</td>
<td>11.3</td>
<td>14.7</td>
<td>0.05</td>
<td>0.01</td>
<td>2.04</td>
<td>3.52</td>
<td>0.35</td>
<td>0.05</td>
<td>&lt;0.1</td>
<td>0.01</td>
<td>73.3</td>
<td>0.24</td>
<td>150</td>
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</tr>
<tr>
<td>G3 (WR)</td>
<td>19.7</td>
<td>14.5</td>
<td>1.4</td>
<td>0.04</td>
<td>2.88</td>
<td>3.68</td>
<td>0.52</td>
<td>0.11</td>
<td>2</td>
<td>0.06</td>
<td>71.7</td>
<td>0.31</td>
<td>160</td>
<td>2.53</td>
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</tr>
<tr>
<td>G4 (UWR)</td>
<td>22.2</td>
<td>12.7</td>
<td>1.93</td>
<td>0.03</td>
<td>1.8</td>
<td>3.73</td>
<td>0.37</td>
<td>0.02</td>
<td>2.6</td>
<td>0.04</td>
<td>78.7</td>
<td>0.23</td>
<td>130</td>
<td>0.38</td>
<td></td>
</tr>
</tbody>
</table>

† SAP, saprolite; UWR, unweathered rock; WR, weathered rock.

### Table 2. Results of sulfur and carbonate analyses.

<table>
<thead>
<tr>
<th>Depth</th>
<th>Profile zone†</th>
<th>sulfur, wt. %</th>
<th>calcite, %</th>
<th>Depth</th>
<th>Profile zone</th>
<th>sulfur, wt. %</th>
<th>calcite, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>SOIL</td>
<td>0.00647 ± 0.00664</td>
<td>0.03818 ± 0.00409</td>
<td>6.8</td>
<td>SAP (G1)</td>
<td>0.00156 ± 0.00106</td>
<td>0.01093 ± 0.00082</td>
</tr>
<tr>
<td>0.5</td>
<td>SOIL</td>
<td>0.00869 ± 0.01370</td>
<td>0.12374 ± 0.03035</td>
<td>11.3</td>
<td>SAP (G2)</td>
<td>0.00074 ± 0.00058</td>
<td>0.01093 ± 0.00082</td>
</tr>
<tr>
<td>0.75</td>
<td>SAP</td>
<td>0.00613 ± 0.00184</td>
<td>2.25532 ± 0.05383</td>
<td>19.7</td>
<td>WR (G3)</td>
<td>0.00109 ± 0.00077</td>
<td>0.01093 ± 0.00082</td>
</tr>
<tr>
<td>0.9</td>
<td>SAP</td>
<td>0.00091 ± 0.00061</td>
<td>2.25532 ± 0.05383</td>
<td>20.3</td>
<td>WR</td>
<td>0.00029 ± 0.00126</td>
<td>0.01093 ± 0.00082</td>
</tr>
<tr>
<td>1</td>
<td>WR</td>
<td>0.00000 ± 0.00000</td>
<td>0.0135 ± 0.00000</td>
<td>21.3</td>
<td>UWR</td>
<td>0.00750 ± 0.00000</td>
<td>0.01093 ± 0.00082</td>
</tr>
<tr>
<td>1.03</td>
<td>WR (D1)</td>
<td>0.00152 ± 0.00121</td>
<td>0.03283 ± 0.00110</td>
<td>22.2</td>
<td>UWR (G4)</td>
<td>0.00324 ± 0.00071</td>
<td>0.01093 ± 0.00082</td>
</tr>
<tr>
<td>1.1</td>
<td>WR</td>
<td>0.00030 ± 0.00012</td>
<td>0.00030 ± 0.00000</td>
<td>23.4</td>
<td>Parent‡</td>
<td>0.00537 ± 0.00050</td>
<td>0.01093 ± 0.00082</td>
</tr>
<tr>
<td>1.2</td>
<td>WR</td>
<td>0.00030 ± 0.00000</td>
<td>0.00030 ± 0.00000</td>
<td>25.8</td>
<td>Parent§</td>
<td>0.00699 ± 0.00200</td>
<td>0.02560 ± 0.00017</td>
</tr>
<tr>
<td>1.4</td>
<td>WR</td>
<td>0.00000 ± 0.00000</td>
<td>0.00000 ± 0.00000</td>
<td>27.5</td>
<td>Parent</td>
<td>0.00256 ± 0.00017</td>
<td>0.02560 ± 0.00017</td>
</tr>
</tbody>
</table>

† SAP, saprolite; SOIL, soil; UWR, unweathered rock; WR, weathered rock.
‡ Parent composition for granite is the two deepest samples (21.3 and 22.2 m) for S data. For calcite data, parent composition is assumed to be the same as the deepest sample (at 22.2 m).
§ Parent composition for diabase was calculated as the average of the four deepest samples (from the depth interval from 2 to 2.75 m).
in scattering patterns, the calculated total nanoporosity differed only slightly: from 1.5% in UWR to 2.2 ± 0.5% (average in WR) (Table 3). In addition, as shown in Table 3, little difference was observed between the fractions of total and unconnected porosities in the two zones. Specifically, in the diabase UWR and WR, more than 50% of nanopores were connected.

Similarly, SSA remained the same within error between the UWR and WR (Table 3). Therefore, despite the development of pores attributed to the weathering, no differences in either porosity or SSA between UWR and WR were calculated (Fig. 6a). Apparently, 2D scattering patterns are more sensitive to spatial distribution of pores than the quantification of total porosity and SSA.

**Porod Exponents and Fractal Dimensions**

Log-log plots of scattering intensity ($I$) vs. scattering vector ($Q$) for diabase samples are shown in Fig. 7a. The negative slope of the linear portion of a log($I$)-log($Q$) plot is called the Porod exponent, $m$. If the plot is linear over several orders of magnitude, $m$ can be used to determine the fractal nature of the distribution of scattering objects (Radlinski, 2006). Specifically, when $3 < m < 4$, the distribution of scatterers is described as a surface fractal. In rocks, such a surface fractal can sometimes be attributed to surface irregularities and other roughness features at the grain–pore interface (Navarre-Sitchler et al., 2013; Jin et al., 2011; Mildner and Hall, 1986). In contrast, values of the slope between 2 and 3 characterize a mass fractal (Anovitz et al., 2009). The fractal dimension for a surface fractal is equal to $D_s = 6 - m$, and for a mass fractal $D_m = m$. According to the definition of these fractals, a rock cube of edge-length $L$ is a surface fractal if its surface area scales as $L^{D_s}$ where $2 < D_s < 3$, while the cube is a mass fractal if its mass scales as $L^{D_m}$ where $2 < D_m < 3$. When scattering from an igneous rock documents a mass fractal, scatterers have been inferred to be pores distributed on grain boundaries and triple junctions (Navarre-Sitchler et al., 2013).

For unweathered and weathered diabase samples, the log-log plots of $I$ vs. $Q$ revealed ranges in the data that are linear over at least 2 orders of magnitude, that is, indicative of a fractal. However, we observed a break in slope at $Q \sim 10^{-3}$ Å$^{-1}$ that correlates with a change from a mass fractal at low $Q$ (larger scatterers) to surface fractal (smaller scatterers) at high $Q$ (Fig. 7a, Table 4).
This behavior is exhibited in both the diabase unweathered and weathered samples: the break in slope occurs at approximately $Q = 10^{-3} \text{ Å}^{-1}$. Above this value of $Q$ (small scatterers), $m \approx 3.4$, and the network of scatterers is a surface fractal, but below this value (large scatterers), the network is a mass fractal ($m \approx 2.9$).

Furthermore, across the transition from UWR to WR in the diabase, both the values for $D_m (= 2.9)$ and $D_s (= 2.6)$ remain relatively unchanged. Therefore, early alteration of the diabase does not change the fractal nature of the rock. In addition, not only is the total porosity (Table 4, Fig. 7b, left) characterized by two fractals, but the $D_2$O/H$_2$O experiment revealed that unconnected pores (Fig. 7b, right) are also characterized by two fractals: a mass fractal with dimension between 2.9 and 3.0 and a surface fractal with dimension between 2.5 and 2.6.

Such breaks in slope in log $I$ – log $Q$ plots were observed previously for other unweathered igneous rocks (Table 5). In those other systems, once again the surface and the mass fractals were related to smaller and larger features, respectively (Buss et al., 2013; Navarre-Sitchler et al., 2013). In contrast, no break in slope was observed for scattering from unweathered shale (Jin et al., 2013; Jin et al., 2011; Hall et al., 1986). Apparently, this indicates that scattering from pores and bumps on surfaces in the shale is not different in terms of fractal dimension; that is, the pores are distributed similarly to the surface irregularities for shale where the particle size is generally less than a few micrometers.

### Pore Size Distribution

In unweathered diabase the volume-weighted pore size distribution showed a peak for diameters of pores of 10 to 20 nm (Fig. 6b). Some 30- to 70-nm pores were also present. In WR diabase, the peak pore size increased, as did the prevalence of larger pores (100–500 nm).

In summary, neutron measurements show that for the diabase (i) an anisotropic nanopore network develops in the WR; (ii) total nanoporosities, SSA of the nanoporosity, and connected nanoporosities in the UWR and WR show no significant differences; (iii) pore sizes in the WR are larger than those in the UWR; and (iv) the pore-grain surface inside both weathered and unweathered diabase is characterized as a surface fractal at high $Q$ (i.e., with scatterer dimensions of ~300 nm) and as a mass fractal at low $Q$ (with scatterer dimensions from ~300 nm to ~1 μm).

### Table 3. Results of neutron experiments.

<table>
<thead>
<tr>
<th>Sample name (profile zone)†</th>
<th>Depth (m)</th>
<th>Density (g cm$^{-3}$)</th>
<th>Neutron SLD (10$^{-6}$ cm$^{-2}$)</th>
<th>Nanoporosity, %</th>
<th>Total Connected (SSA, m$^2$ g$^{-1}$) Unconnected</th>
<th>Total Connected (SSA, m$^2$ g$^{-1}$) Unconnected</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diabase</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D1 (WR)</td>
<td>1.03</td>
<td>2.98</td>
<td>4.200</td>
<td>1.96</td>
<td>1.06</td>
<td>0.90</td>
</tr>
<tr>
<td>D2 (WR)</td>
<td>1.8</td>
<td>3.00</td>
<td>4.170</td>
<td>2.74</td>
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<td>0.72</td>
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<tr>
<td>D3 (WR)</td>
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<td>3.00</td>
<td>4.186</td>
<td>1.96</td>
<td>0.59</td>
<td>1.37</td>
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<tr>
<td>D4 (UWR)</td>
<td>2.75</td>
<td>3.00</td>
<td>4.185</td>
<td>1.54</td>
<td>0.72</td>
<td>0.82</td>
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<td>Granite</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1 (SAP)</td>
<td>6.8</td>
<td>1.51</td>
<td>3.995</td>
<td>7.96</td>
<td>1.16</td>
<td>6.80</td>
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<td>G2 (SAP)</td>
<td>11.3</td>
<td>1.69</td>
<td>3.995</td>
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<td>4.41</td>
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<td>G3 (WR)</td>
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<td>2.00</td>
<td>3.958</td>
<td>9.47</td>
<td>1.65</td>
<td>7.82</td>
</tr>
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<td>G4 (UWR)</td>
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<td>2.60</td>
<td>3.991</td>
<td>2.06</td>
<td>0.62</td>
<td>1.44</td>
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</table>

† SAP, saprolite; SOIL, soil; UWR, unweathered rock; WR, weathered rock.

‡ SLD, scattering length density.

§ SSA, specific surface area.

---

**Fig. 6.** (a) Connected (yellow circles) and isolated (black circles) porosity and surface area of diabase determined from small-angle neutron scattering (SANS)–ultra-small-angle neutron scattering (USANS). (b) Volume weighted pore size distribution, $f(r)$, for total pores in diabase. It is defined as the number of pores within the narrow size (diameter) interval between $r$ and $r + dr$, $N(r, r + dr)$, divided by the total number of pores, $N$: $f(r) = N(r, r + dr)/N$. In simple terms, $f(r)$ is the proportion of pores of diameter within a narrow band centered on $r$ within the total population of pores. The pore size distribution, $f(r)$, was computed from SANS–USANS data for each sample using the standard Spherical Pore Approximation procedure (Radlinski, 2006). The Q-range for pore size distribution fitting was from $3.1 \times 10^{-5}$ Å$^{-1}$ to 0.13 Å$^{-1}$. SAP, saprolite; SOIL, soil; SSA, specific surface area; UWR, unweathered rock; WR, weathered rock.
Unlike the diabase, the two-dimensional patterns of scattered intensity observed for all granite samples (not shown here) were isotropic: scattering was equally intense in all azimuthal directions similar to UWR diabase pattern (Fig. 5a). Thus, in the granite, scatterers were either shaped or distributed in an isotropic fashion throughout the weathered rock.

Nanoporosity and Specific Surface Area

In contrast to the diabase where little change in nanoporosity was observed from UWR to WR, the total nanoporosity in the granite sharply increased from 1.5% in the UWR to 9.5% in the WR. However, the porosity decreased in the granite SAP (Table 3) (note that no sample of diabase SAP was measured with NS).

The granite was similar to the diabase in that the connected porosity in the WR and SAP increased only slightly compared to the UWR: connected porosity remains <2% as weathering progresses (Fig. 8a, left). In fact, the fraction of connected–total porosity in unweathered samples (0.3) decreased to 0.17 for at the WR–UWR interface, 0.22 at the SAP–UWR interface, and 0.15 in the SAP.

The total SSA in the granite increased upward toward the surface: the SSA of unweathered granite was three to four times smaller than that of SAP samples. Furthermore, whereas most of the SSA in the diabase WR was not measured on connected pores, most of the SSA in the granite WR was measured on connected pores. In contrast, most of the SSA in the granite SAP zone was unconnected (Fig. 8a, right).

Pore Size Distribution

In the unweathered granite (G4-UWR), most of the pores are unconnected; the scattering from unconnected pores was slightly lower than scattering from all pores when inspected over the whole Q-range (Fig. 8b). This discrepancy was particularly large for scattering in the mid-Q range (2 × 10⁻⁴ < Q < 2 × 10⁻³ Å⁻¹). This is consistent with a small con-
Distribution from connected pores throughout the whole Q-range but especially for pores in the range of 300 to 1200 nm. However in the WR zone, these connected mid-Q pores start to close up at the same time that smaller 3- to 10-nm pores become more connected (Fig. 8b). As weathering progressed upward from G4 to G3, this trend of losing large-pore connected porosity continues; larger pores (10–100 nm) disappear from the material while smaller pores (3–10 nm) persist (Fig. 8c). It is important, however, to note here that large pores could disappear either by (i) infilling or (ii) growth into larger pores, which are no longer detectable with neutron scattering (i.e., larger than 10 \( \mu \)m).

In contrast to the observations for total porosity in the WR, the unconnected porosity distribution lacks the peak at 5 to 6 nm (Fig. 8c). The observations from scattering curves (Fig. 8b) and porosity distributions (Fig. 8c) are consistent with connectivity only for the smallest pores (<10 nm) in the WR zone. These small pores are not abundant enough to contribute significantly to the total porosity (Fig. 8a, left). However, due to their small size, they comprise the majority of the total SSA (Fig. 8a, right, Table 3).

**Porod Exponents and Fractal Dimensions**

The log-log plots of \( I \) vs. \( Q \) for granite samples are shown in Fig. 9a. Similar to the unweathered diabase, the UWR granite also exhibited a break in slope at \( Q \sim 1 \times 10^{-3} \text{ Å}^{-1} \). In addition, the scatterer network was characterized as a mass fractal at low \( Q \) and a surface fractal at higher \( Q \). After weathering, in contrast, all the granite samples (WR and SAP) were surface fractals (\( m > 3 \)) over the whole \( Q \)-range (i.e., no break in slope [Fig. 9a]). Furthermore, the surface fractal dimensions do not change significantly with depth: \( D_s \) varies from 2.6 in the UWR to 2.7 in WR to 2.8 in SAP (Table 3).

Summarizing these findings for granite, we observe (i) the nanopore-grain interface inside the granite always scatters isotropically; (ii) both the total nanoporosity and the SSA of this porosity increases greatly from UWR to WR; (iii) the connected nanoporosity is comprised dominantly of pores <10 nm diam.; and (iv) scattering occurs both from mass and surface fractals in the unweathered parent material but only from a surface fractal in weathered material.

### Table 5. Fractal dimensions of different rock types, measured by neutron scattering.

<table>
<thead>
<tr>
<th>Rock type/sample type</th>
<th>Fractal dimensions†</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Quartz diorite corestone/Individual sections cut from rindlets at different distance from the core</td>
<td></td>
<td>Navarre-Sitchler et al., 2013</td>
</tr>
<tr>
<td>Unweathered</td>
<td>2.98 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>Weathered</td>
<td>2.80 ± 0.07</td>
<td></td>
</tr>
<tr>
<td>2. Basaltic andesite/clast with weathering ring</td>
<td></td>
<td>Navarre-Sitchler et al., 2013</td>
</tr>
<tr>
<td>Unweathered</td>
<td>2.90 ± 0.07</td>
<td></td>
</tr>
<tr>
<td>Weathered</td>
<td>2.78 ± 0.15</td>
<td></td>
</tr>
<tr>
<td>3. Rose Hill shale</td>
<td></td>
<td>Jin et al., 2011</td>
</tr>
<tr>
<td>Drill cores</td>
<td>2.93 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Shale chips in soil profile SSRT</td>
<td></td>
<td>Navarre-Sitchler et al., 2013</td>
</tr>
<tr>
<td>Weathered</td>
<td>2.82 ± 0.04; 2.77± 0.00</td>
<td></td>
</tr>
<tr>
<td>Shale chips in soil profile SPRT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weathered</td>
<td>2.87 ± 0.00; 2.83 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>4. Marcellus shale (Oakta Creek member)/Shale chips in soil profile</td>
<td></td>
<td>Jin et al., 2013</td>
</tr>
<tr>
<td>Weathered</td>
<td>2.81 ± 0.12</td>
<td></td>
</tr>
<tr>
<td>Unweathered</td>
<td>2.97 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>Weathered</td>
<td>2.76 ± 0.08</td>
<td></td>
</tr>
</tbody>
</table>

† Surface fractals are shown in italic; all others are mass fractals.
‡ Surface fractals are observed at the top of both soil profiles (SSRT and SPRT). SSRT, south swale ridge top; SPRT, south planar ridge top (Jin et al., 2011).

![Fig. 8. A. Connected (yellow circles) and isolated (black circles) porosity and surface area of granite determined from small-angle neutron scattering (SANS)–ultra-small-angle neutron scattering (USANS).](image-url)

(b) SANS–USANS scattering curves for UWR and WR granite. Black line: dry measurements (total porosity); grey line: wet measurements (unconnected pores). The difference between the two curves how connected porosity. (c) Volume weighted pore size distribution, \( f(r) \), for total (dry) and isolated (wet) pores in diabase. SAP, saprolite; SOIL, soil; UWR, unweathered rock; WR, weathered rock.
**MEPOROSITY AND STRAIN IN GRANITE AND DIABASE**

Measurements of mesoporosity ($3 \mu m < d < 0.5 \text{ mm}$), that is, porosity quantified from μ-CT images for diabase and granite, are presented in Table 6. In the UWR diabase, the total mesoporosity was very low, and pores were imaged to be generally equant. However, the mesoporosity measured on separate pyroxene grains (1.5%) was observed to be larger than for individual plagioclase grains (0.05%). In the WR zone, the pyroxene mesoporosity increased to 6 to 7%. This value was not observed to vary significantly with depth below the SAP zone. The large standard deviation in mesoporosity reflects the large variations observed for different subareas, presumably due to variation in pyroxene content. Plagioclase porosity also increases from UWR to WR zone; however, pyroxene porosity is larger than that in plagioclase in all samples in the WR zone. These observations are consistent with the conclusion that pyroxene weathering initiates before plagioclase dissolution in the WR—a conclusion also reached based on microscopy (Fig. 5b). Although the pyroxene contains Fe (see discussion below), no Fe-hydroxide precipitation was observed. The total mesoporosity—low in both the diabase UWR and WR—increased to ~25% in the lower saprolite at 0.9 m (sample F19–2C). Then it decreased to ~12% at 0.75 m (sample F19–2A), (Table 6).

For granite, total mesoporosity includes both equant pores and fractures. This mesoporosity was low in the UWR granite (~2%). Where mesofractures were observed under μ-CT, they were mostly associated with biotite grains (Fig. 10). Mesoporosity increased markedly to ~30% in WR but then decreased in the SAP zone (Table 6). Overall, granite saprolite showed more variability in mesoporosity (i.e., both high and low porosity regions were observed) than was observed in the WR.

**Table 6. Mesoporosity ($3 \mu m < d < 1 \text{ mm}$) in diabase and granite as determined from microcomputed tomography.**

<table>
<thead>
<tr>
<th>Sample name (profile zone)†</th>
<th>Depth, m</th>
<th>Mesoporosity, v/v</th>
<th>Na</th>
<th>Mg</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diabase</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F19-2A (SAP)</td>
<td>0.75</td>
<td>11.8 ± 4.3</td>
<td>−0.90</td>
<td>−0.91</td>
<td>−0.93</td>
</tr>
<tr>
<td>F19-2C (SAP)</td>
<td>0.9</td>
<td>25.5 ± 6.9</td>
<td>−0.05</td>
<td>−0.07</td>
<td>−0.38</td>
</tr>
<tr>
<td>D1 (WR)</td>
<td>1.03</td>
<td>1.3 ± 0.5% (Pl), 7.3 ± 5.2 (Pyr)‡</td>
<td>No depletion</td>
<td>No depletion</td>
<td>−0.18</td>
</tr>
<tr>
<td>D1 (WR)</td>
<td>1.8</td>
<td>1.8 ± 1.5% (Pl), 5.9 ± 4.2 (Pyr)</td>
<td>No depletion</td>
<td>No depletion</td>
<td>−0.04</td>
</tr>
<tr>
<td>D3 (WR)</td>
<td>2</td>
<td>1.0 ± 0.7% (Pl), 6.2 ± 3.8 (Pyr)</td>
<td>No depletion</td>
<td>No depletion</td>
<td>No depletion</td>
</tr>
<tr>
<td>D4 (UWR)</td>
<td>2.75</td>
<td>0.05 ± 0.01% (Pl), 1.5 ± 0.8 (Pyr)</td>
<td>No depletion</td>
<td>No depletion</td>
<td>No depletion</td>
</tr>
<tr>
<td>Granite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1 (SAP)</td>
<td>6.8</td>
<td>12.5 ± 4.9</td>
<td>−0.97</td>
<td>−0.10</td>
<td>−0.76</td>
</tr>
<tr>
<td>G2 (SAP)</td>
<td>11.3</td>
<td>18.4 ± 6.3</td>
<td>−0.98</td>
<td>−0.09</td>
<td>−0.83</td>
</tr>
<tr>
<td>G3 (WR)</td>
<td>19.7</td>
<td>30.4 ± 0.2</td>
<td>−0.44</td>
<td>−0.04</td>
<td>−0.84</td>
</tr>
<tr>
<td>G4 (UWR)</td>
<td>22.2</td>
<td>1.9 ± 0.75</td>
<td>No depletion</td>
<td>No depletion</td>
<td>No depletion</td>
</tr>
</tbody>
</table>

† SAP, saprolite; UWR, unweathered rock; WR, weathered rock.
‡ For diabase WR and UWR zone porosity was determined separately on plagioclase (Pl) and pyroxene (Pyr). At least 5 measurements were taken for each mineral.
§ For G4 (UWR) mesoporosity includes both round-like pores and fractures.
Strain

Trends in porosity may be related to volume changes in the rock during weathering. The strain is defined as the extent of change of volume of weathered material ($V_w$) with respect to the original volume, $V_p$ (Brimhall and Dietrich, 1987; Egli and Fitze, 2000):

$$
\varepsilon_{Ti,w} = \frac{V_w - V_p}{V_p} = \frac{\rho_p C_{Ti,p}}{\rho_w C_{Ti,w}} - 1
$$

where $C_{Ti,w}$ and $C_{Ti,p}$ are concentrations of an element $i$ in weathered and parent material, respectively. Here, $C_{Ti,p}$ and $C_{Ti,w}$ are concentrations of an immobile element (here, Ti), and $\rho_p$ and $\rho_w$ are densities in weathered (subscript $w$) and parent (subscript $p$) material, respectively. In strain calculations for both diabase and granite, we considered the average of the densities of the two deepest samples as the density of parent material (samples D4 and D3 for diabase, and samples G4 and F-11-I, see Tables AI and AII in Bazilevskaya et al., 2013). Negative strain values indicate that the volume of the original protolith decreases in weathered material and positive values indicate expansion in volume (isovolumetric weathering means strain = 0). Changes in volume due to compaction or expansion from chemical and physical weathering, addition of organic matter, or bioturbation can be significant (Schaeztl and Anderson, 2005).

In both diabase and granite profiles, strain was positive in the lower saprolite zone (expansion), then decreased to 0 in the upper SAP. In the Soil, strain decreased to <0 (compaction) (Fig. 2; Fig. 11). The increase in volume in the diabase SAP coincides with the increase in mesoporosity, with onset of plagioclase dissolution (Table 6, Fig. 2) and formation of expandable clays such as smectite (Pavich et al., 1989). Similarly, the volume increase in the granite is also observed within the plagioclase reaction front (Table 5, Fig. 2b).

DISCUSSION

Mechanism of Weathering Reactions in Diabase

The first weathering reaction in the diabase (observed in the WR zone) was pyroxene dissolution. This reaction was documented both by SANS and USANS (anisotropy of scattering pattern) and microscopy (Fig. 5). Eventually, plagioclase dissolution initiates and in the transition from WR to SAP, the mesoporosity of plagioclase and pyroxene grains increase at least twofold, although this porosity still remains below 5 to 6% (Table 5). From UWR to WR, the nanoporosity, both total and connected, and SSA increase slightly (Table 3) even though no significant element depletion or oxidation of Fe are observed. The only chemical change that was detected was loss of ferrous Fe ($t_{FeO} = 0.18$) and S, documented at the top of the WR zone (Table 6, Fig. 4). Thus, even before bulk element composition changes measurably, nanoporosity opens in the diabase as the ferrous Fe-containing phase, pyroxene, begins to dissolve. Pyrite dissolution (as indicated by the decrease $t_Ti$ at the WR-SAP interface, Fig. 4) could also contribute to nanoporosity development, but to a lesser extent than pyroxene because of the low pyrite content in the rock.

Even as the pyroxene and plagioclase dissolve, the WR remains a mass + surface fractal like the UWR (Table 4, Fig. 7b). The lack of change in the fractal nature of the diabase between the UWR and the WR indicates that the structure was preserved during this initial stage of weathering. All these observations for the WR diabase (i.e., no major element depletion, no oxidation of ferrous Fe, low porosity, and intact rock structure) are consistent with no change in the dominant transport mechanism between the UWR and the WR since the results imply that oxygen was not able to penetrate into this portion of the rock. In other words, the transport mechanism for solutes in the UWR is likely the same as in the samples up to the WR-SAP boundary that were investigated with neutron scattering—and given the low porosity, this mechanism is likely diffusion rather than pore fluid advection. Finally, all these samples are likely to have weathered mostly beneath the water table, which has been reported to lie within the saprolite zone in this region (Bazilevskaya et al., 2013; Cleaves, 1993; Pavich et al., 1989).

A sharp increase in mesoporosity in the SAP zone compared to the UWR and WR zones (Table 5, Fig. 12a) coincides with onset of more significant plagioclase and pyroxene dissolution. This dissolution proceeds until Na, Mg, and FeO are almost completely depleted within 0.75 m of the surface (Fig. 3, Table 5). Here, the reaction front (i.e., the depth zone over which reaction occurs) is very narrow (0.25 m = 1 m – 0.75 m). Since diffusion of O$_2$ is fast in air-filled pores but very slow in water-filled pores below the water table (Bornstein et al., 1980), nonoxidative dissolution of pyroxene likely took place beneath the water table in the WR. In contrast, oxidative dissolution appears to have dominated above the groundwater table where
pores are filled with O₂-rich air rather than water. The oxygenated environment in the SAP is documented by immobilization of Fe by precipitation of Fe(III) (oxy)hydroxides as inferred from oxidized FeO (Fig. 2), which is in agreement with microscopic observations (Pavich et al., 1989).

Formation of another secondary mineral, the Fe-rich smectite nontronite, has also been reported in this rock (Bazilevskaya et al., 2013; Pavich et al., 1989). Smectite is a swelling clay; the transformation of pyroxene to smectite can occur with an increase in net rock volume due to smectite swelling (\(P_{\text{prod}}/P_{\text{react}} > 1\)) (Velbel, 1989). Nontronite comprises ~20 v/v of the regolith in the lower saprolite at 0.9 m. Consistent with this, a high positive value for strain (\(e_{w} > 0\)) was calculated at the 0.9-m depth where the smectite content reached 20% (Fig. 2) The precipitation of secondary minerals such as smectite may explain the spatial variability in porosity in diabase SAP zone (Table 6). In the absence of O₂, pyroxene likely dissolves due to proton-promoted dissolution. For example, a simplified reaction describing the dissolution of augite via this mechanism could be written as:

\[
\begin{align*}
\text{Ca}_{0.34}\text{Fe}_{0.22}\text{Mg}_{0.44}\text{Si}_{0.34}\text{O}_{8} \text{(augite)} + 4\text{H}^+ &\rightarrow \\
0.34\text{Ca}^{2+} + 0.22\text{Fe}^{2+} + 0.44\text{Mg}^{2+} + 2\text{SiO}_2\text{(aq)} + 2\text{H}_2\text{O} &\rightarrow
\end{align*}
\]

(6)

Since the Fe content in diabase is high, precipitation of significant amounts of Fe (oxy)hydroxides in the O₂-rich SAP zone is expected. Such precipitates will likely reduce the permeability and diffusivity of the rock, thus blocking available fluid pathways for removing dissolved cations. Under such conditions, precipitation of other secondary phases such as Al-hydroxides and smectites are likely. In such a system, it is common to see spatial variability in porosity, reactive surface area, and local fluid supersaturation (Jamtveit et al., 2009; Putnis, 2002; Merino et al., 1993), all of which may document variability in available O₂ in the pore fluid space.

In such a fluid-saturated, low-flow environment that is charged with significant partial pressures of CO₂, dissolution of silicates will drive up the alkalinity and pH of the pore fluid, producing high concentrations of the carbonate ion (Brantley et al., 2014). In addition, if Ca is also being released to solution during dissolution, calcite can precipitate. Other researchers (Drake et al., 1989).
al., 2008), for example, reported calcite precipitation at depth in granites above a zone of oxidation that presumably released Ca ions to solution. Consistent with this, calcite enrichment is observed in the SAP zone (Fig. 4a, note the break in the range plotted in the x axis) in the diabase profile. Carbonate precipitation is attributed to dissolution of plagioclase and pyroxene and the release of Ca and Mg ions under conditions of minimally flowing CO$_2$-charged fluid under fluid-saturated conditions, that is, consumption of CO$_2$ drives pH to elevated values in microenvironments. A simplified reaction for calcite precipitation under neutral or slightly alkaline conditions can be written as follows:

$$\text{Ca}^{2+} + 2\text{HCO}_3^- \leftrightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$$

According to this reaction, at high values of pH where bicarbonate ions predominate, a decrease in pCO$_2$ favors calcite formation. Calcite precipitation higher in the profile is likely hindered because CO$_2$-charged fluids advect in the soil because of the increase in weathering-induced porosity, thus maintaining a more nearly constant and lower pH. As the porosity (and by inference, permeability) decreases with depth, advection slows and CO$_2$ dissolved in water is consumed by silicate dissolution. According to this argument, calcite precipitation may in some cases document the depth where the mechanism of solute transport changes from advection to diffusion (this is also the zone [or depth] where depletion of CO$_2$ and O$_2$ begins).

In summary, the interplay of porosity and mineral reactions for diabase is shown in Fig. 12. The connected nanoporosity and SSA of the nanoporosity documents the dissolution of the first mineral: pyroxene. This dissolution is anisotropic with respect to scattering and is due to dissolution of exolution lamellae (Fig. 5). The loss of S in this zone could indicate that pyrite is dissolving oxidatively, using up the low concentration of O$_2$, which diffuses in, producing slightly acidic fluids that initiate the weathering of pyroxene. Early dissolution of pyroxene proceeds beneath the water table in the absence of O$_2$ most likely via a proton-promoted mechanism, as indicated by the lack of Fe(III) oxide precipitation in this zone. These reactions are followed by dissolution of plagioclase within the WR, resulting in a slight increase in mesoporosity. Such weathering can occur deep in the rock because there are connected nanopores present in the UWR (Fig. 6).

Oxygen is depleted in the downward percolating waters presumably via the oxidative reactions occurring higher in the saprolite. The diabase is a massive rock with only limited fractures; thus, the main mechanism of solute transport within this zone is molecular diffusion rather than flow. Consistent with both of these, the diabase starts and remains a mass + surface fractal throughout the WR zone.

This is consistent with the results of numerical modeling of the diabase profile presented by Bazilevskaya et al. (2013) where solute transport during weathering was assumed to be dominated by diffusion. The reaction zone for plagioclase and pyroxene are both very thin, that is, 0.5 m, consistent with diffusive rather than advective transport of reactants. In addition, the WR zone lies below the water table (Pavich et al., 1989) where O$_2$ diffusion in water-saturated pores is expected to be very slow. As a result, the final consumption of O$_2$, as indicated by the zone of pyrite oxidation, lies higher than the zone of proton depletion (pyroxene dissolution). In contrast, in the SAP, a series of dissolution-precipitation reactions takes place that lead to a dramatic increase in mesoporosity, which in turn results in advection of pore fluids into or through this zone. The large variations in mesoporosity within the SAP zone are likely due to precipitation of secondary minerals as observed by Pavich et al. (1989).

**Sequence of Weathering in the Granite**

It is known that the first mineral to weather in granite is often biotite (Buss et al., 2008; Cassiaux et al., 2006; Fletcher...
et al., 2006; Sardini et al., 2006; Robert et al., 2003; Graham and Francovizcaino, 1992; Eggler et al., 1969). Indeed, it has long been known that oxidation or cation exchange reactions in biotite during weathering can cause expansion and fracturing in crystalline rocks (Bisdom et al., 1982; Rodgers and Rodgers, 1848). In the Piedmont granite, we observed fractures induced by biotite oxidation in the UWR zone (Bazilevskaya et al., 2013). Formation of these fractures is likely to increase the permeability, which favors advection of reactive fluids containing O2 and CO2 into the granite UWR, well below the groundwater table, which has been inferred to lie in the saprolite (Cleaves, 1993; Pavich, 1986; Sowers, 1963). This conceptual model is consistent with the depth of the first two reactions observed in the granite-FeO depletion and immobilization as Fe(III) hydroxide in UWR zone as deep as 21 m below the surface (Fig. 2).

Such biotite-driven microfracturing could likely lead to an increase in the granite permeability, and, therefore, to the increased plagioclase dissolution in the WR (Fig. 2). This dissolution is documented by increases in both nano and mesopores (Fig. 8a; Fig. 12b). Furthermore, the intact granite UWR transformed from a mass + surface fractal to a surface fractal in WR and SAP zones (Fig. 9b). For a surface fractal, a Porod exponent $m$ of 3 ($D_s = 3$) is consistent with a very rough surface while $m = 4$ indicates a very smooth surface ($D_s = 2$) (Radlinski et al., 1999). For the granite, the Porod exponent $m$ decreased from 3.4 in the UWR zone to 3.2 in the SAP zone (Table 4, Fig. 9b). In other words, the surface became rougher as weathering progressed in the SAP.

Interestingly, although mesoporosity was higher in the unweathered granite than in the UWR diabase (Table 6), the nanopores in the weathered granite are less connected than in the WR diabase. Also, although nanoporosity increased significantly in the WR zone compared to the UWR, presumably due to biotite-caused fracturing and plagioclase dissolution (Fig. 10), only pores $<10$ nm were connected (Fig. 8b and 8c). We may conclude that because of limited connectivity, most of the nanopores played only a minor role in the weathering reactions except for their role in allowing O2 to enter via diffusion, thus resulting in the oxidation and fracturing of biotite. It is then these fractures that allow water to infiltrate through the mesopores without changing the nanopores significantly. Thus, the nanoporosity is effectively bypassed. Indeed, the reaction front for silicates in the granite lies higher than the reaction front for oxidation (Brantley et al., 2014). Numerical modeling suggested that advective transport dominated in granite (Bazilevskaya et al., 2013), thus creating a very thick reaction zone for plagioclase (Fig. 2b) and thick weathering profile.

### Main Factors Affecting Diabase and Granite Weathering in the Piedmont

In general, deep weathering is controlled by (i) characteristics of the rock (e.g., mineral and chemical composition, grain size, porosity), (ii) properties of the reactive fluid (e.g., composition, ionic strength, acidity, temperature), and (iii) the flow characteristics of the fluid. All these factors are related to each other so that any variation in one of them leads to changes in the others. We summarize some of the important features below.

#### Rock Characteristics

Mineral composition and texture of a parent rock greatly affect its reaction with fluid. With respect to rock composition, diabase and granite have minerals with different degrees of “alter-ability.” Fast-reacting Fe-Mg-bearing minerals are more abundant in a diabase than granite. In fact, in the granite, the quartz and K-feldspar do not contribute to the formation of clay minerals (quartz) or are relatively resistant to chemical weathering (quartz and K-spars). Parent rock composition also controls the formation of secondary minerals. For example, clay production, that is, the amount of clays produced in the weathered zone, depends on the MgO content of the parent rock (Velde and Meunier, 2008). This could be related to the enhancing effect of Mg ions for nucleation and growth of clay minerals (Grauby et al., 1993; Grauby et al., 1994). In granite, plagioclase weathers to kaolinite and in diabase, plagioclase weathers to smectite. The extent of accumulation of secondary phases is thus controlled by the fluid chemistry and its velocity. The lower fluid velocity in the unfractured diabase leads to higher cation concentrations in pore water, which obviously favors secondary clay formation. Indeed, more clays form on diabase than on granite (Pavich et al., 1989).

In comparison to composition, the grain size and pore network structure apparently are even more important because they control the mechanism of reactive fluid transport. According to several authors (Ballesteros et al., 2010; Meunier et al., 2007), three systems of weathering have been identified: (i) contact microsystems (pore dimensions on the order of Å or nanometers), (ii) plasmic microsystems (pore dimensions nanometers–micrometers), and (iii) fissure systems (pore dimensions micrometers–centimeters). In contact and plasmic microsystems, diffusion is the primary mechanism of solute transport (Brady and Weil, 2007; Nahon, 1991).

These three systems are exemplified here in our observations. The neutron scattering from the diabase documented both a surface fractal at high Q (pore diameter 1–300 nm) and mass fractal at low Q (~300 nm to ~5 μm). In the unweathered rocks, the mass fractal is comprised of scatterers of dimension of 1 to 300 nm, that is, similar to contact microsystems. In contrast, the surface fractal consists of scatterers of dimensions from 300 nm to ~5 μm, that is, consistent with plasmic microsystems. Our observations are consistent with the conclusion that, when a low-porosity rock retains both the mass + surface fractals during weathering, that is, it still preserves its initial structure, solute transport is mostly by diffusion. In contrast, when there is transformation from mass + surface to surface fractal, the mechanism of reactive transport changes from diffusion to advection. This transformation occurred in the transition from the UWR to the WR in the granite and was characterized by a wide reaction front for plagioclase, consistent with solute transport by advection.
Properties of the Reactive Fluid

Weathering occurs as rocks dissolve to neutralize and reduce the carbonated, oxidizing fluids found at Earth’s surface (Jamtveit and Hammer, 2012; Brantley, 2010; Graham et al., 2010; Drever and Stillings, 1997). These surficial fluids are acidic and oxidizing because they equilibrate with CO₂ and O₂ in the atmosphere. Rocks consume CO₂ and O₂ to different extents because of both their chemical composition as well as physical properties, such as porosity and permeability. We clearly demonstrate this for the two Virginia weathering profiles. For example, fractures in the protolith and microfractures developed as a result of biotite dissolution in UWR presumably allow pore fluids to infiltrate deep into the granitic material. Even beneath the water table, connected nanopores in the granite allow O₂ access to biotite grains, which in turn causes the oxidation and fracturing, allowing further infiltration of water. The sequence of primary weathering reactions described above is consistent with the fact that the reaction front for plagioclase dissolution (consumption of protons) lies higher than the reaction front for FeO oxidation (consumption of O₂) (Fig. 2).

In contrast, the dense, massive, and impermeable diabase lacked fractures (Bazilevskaya et al., 2013). In addition, although well-connected anisotropic nanopores are present in the diabase parent rock, O₂ apparently did not permeate significantly into the rock because loss of Fe(II) occurred without precipitation of ferric oxides. Oxygen likely became depleted relatively high in the system because of the high ferrous Fe content of the rock. Thus, even though nanopores are present in this case, little to no O₂ is able to penetrate the rock beneath the point of pyrite dissolution. The argument, therefore, is that oxidation-driven fracturing did not occur in the diabase because the oxidation front lies higher than the silicate dissolution front and volume increases never occurred at depth to fracture the rock (Fig. 2).

Brantley et al. (2014) have hypothesized that these observations may be generally true for weathering of crystalline rocks. Where the initial concentrations of ferrous oxides are higher than the concentrations of alkalis and alkaline earths, O₂ becomes depleted at shallower depths than CO₂ is depleted, and no deep microfracturing occurs. In such rocks—that is, more mafic rocks—deep regolith profiles tend not to form. In contrast, where the starting concentrations of ferrous oxides are low compared to alkalis and alkaline earths, CO₂ becomes depleted at shallower depths than O₂, and deep microfracturing occurs, driving deep infiltration of meteoric fluids and a correspondingly deep regolith. Bazilevskaya et al. (2013) showed that for 27 profiles studied worldwide from ridgetop settings, regolith on granite was deeper than on diabase, consistent with these inferences.

CONCLUSIONS

In the plagioclase reaction zone in both lithologies, mesoporosity (3 μm < d < 0.5 mm), calculated from μ-CT scans, comprised a larger total volume fraction than the nanoporosity. This midscale porosity increased dramatically in the zone of plagioclase dissolution in both rocks; however, in both rocks this porosity significantly decreases towards the surface due to precipitation of secondary clays. The initial increase in mesoporosity in the diabase was driven by coalescence of small pores into larger pores, while the increase in porosity (and by inference, permeability) in the granite was driven by growth of fractures.

Neutron scattering patterns showed that the diabase developed an anisotropic pore network in the weathered rock before disaggregation and before loss of major elements. These anisotropic pores were attributed to dissolution of pyroxene along dissolving exsolution lamellae, the first weathering reaction in the deep diabase. However, even with this dissolution, increases in total nanoporosity and SSA were not detectable when weathered diabase and its protolith (unweathered rock) are compared. In contrast, the deepest reaction observed in granite was oxidation and microfracturing around biotite, which was accompanied by secondary precipitation. Above this early microfracturing, isotropic nanopores increased in concentration to 10% as plagioclase dissolved in the feldspar reaction zone (RZ). In the RZ, larger fractures were also imaged. Most of the SSA in this plagioclase RZ consisted of very small connected nanopores (<10 nm diam.). In contrast, in the upper part of the weathering profile, only a small volume fraction of the nanopores in the granite was connected.

Unlike diabase, granite showed a drastic change in scattering across the plagioclase reaction front, which was recorded by a large increase in both porosity and the mineral–pore interface, and a transition from mass + surface fractals in UWR granite to surface fractal only in WR. However, nanopores in granite had limited connectivity and played a secondary role in triggering dissolution reactions. In contrast, mesopores, particularly fractures developed as a result of biotite oxidation, increased granite permeability to the O₂-rich advective fluid, accelerating plagioclase dissolution below the groundwater table. Connectivity of nanoporosity in diabase was high (>50% connected), but the rock lacked larger mesopores that could have enhanced fluid flow. The slow O₂ diffusion in water-saturated diabase below the groundwater table is another effect that limits pyroxene and plagioclase dissolution.

Neutron scattering also revealed the fractal nature of the granite and diabase porosity. The internal surface of both unweathered rocks was characterized as both a mass fractal for the larger features, that is, scattering from pores along grain boundaries and triple junctions, and a surface fractal for smaller features, that is, scattering from the bumps at the grain–pore interface. For example, the neutron scattering from the diabase documented both a surface fractal at high Q (pore diameter 1–300 nm) and mass fractal at low Q (~300 nm to ~5 μm). The delineation between mass and surface fractals occurred at features of ~200 nm in the unweathered granite. In contrast, as weathering and fracturing occurred in the granite in the plagioclase RZ, scattering documented only surface fractals. The observed surface fractals are consistent with fracturing and disaggregation of the initial granite structure into smaller subunits. The transformation from a mass + surface to a surface fractal in granite suggests transformation from a regime where the bulk of the solute

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transport is by diffusion to a regime where the transport is dominantly advective. The silicate dissolution front was documented at greater depths than the oxidation front in the diabase, whereas the reverse was true in the granitic rock. For the granite, the low ferrous content of the rock likely allowed deep penetration of O$_2$ in nanopores deep into unweathered rock, driving oxidation and microfracturing of biotite. As fractures opened, O$_2$-rich fluids penetrated the rock via advection even below the groundwater table, driving both biotite and plagioclase dissolution. In contrast, the diabase had similar nanoporosity, but did not oxidize at depth or fracture, presumably because O$_2$ was depleted high in the profile of this Fe-rich lithology. Therefore, we attribute the difference in regolith thickness between granite and diabase mainly to the difference in the dominant mode of solute transport which, in turn, depends on different balances in CO$_2$ and O$_2$ consumption. This work documents the importance of fluid flow mechanisms and the consumption of oxygen in controlling the depth of regolith formation.

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