Porosity and surface area evolution during weathering of two igneous rocks

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Abstract
During weathering, pores in rocks release nutrients and store water vital for growth of microbial and plant life. Thus, the growth of rock porosity during the advance of weathering into bedrock is a life-sustaining process for terrestrial ecosystems. Here, we use neutron scattering (NS) to show how porosity grows during initial weathering of two igneous rock compositions. One of the rocks weathers spheroidally while the other does not. The weathering advance rates of the two systems also differ, perhaps due to this difference in mechanism, from 0.24 to 100 mm kyr\(^{-1}\) respectively. The scattering data document how surfaces inside the feldspar-dominated rocks change as weathering advances into the protolith. In the unaltered rocks, neutrons scatter from pores between mineral grains and submicron bumps on pore-grain surfaces: the scattering is described by both a mass and a surface fractal, respectively. In the rock that weathers due to diffusive transport of reactants without spheroidal fracturing, porosity and surface area increase relatively consistently with weathering of plagioclase over a mm-thick reaction front. Across this front, both fractal dimensions decrease, consistent with development of a more monodisperse pore network with smoother pore surfaces. Both changes are consistent largely with increasing connectivity of pores without significant surface roughening. Lack of surface roughening of pore walls is consistent with transport-limited weathering. In contrast, porosity and surface area increase across a many cm-thick reaction front in the spheroidally weathering rock. In that rock, the mass and surface fractals transform during weathering to multiple surface fractals as micro-cracking reduces the size of diffusion-limited subzones of the matrix. Across the reaction front of plagioclase, the surface area and porosity of the diffusion-limited regions only change to a minor extent until the rock disaggregates into saprolite. The different patterns in porosity development of the two rocks are attributed to the presence or absence of spheroidal weathering, and the associated differences in mechanisms of solute transport, i.e. advective infiltration plus diffusion in the rock that spheroidally fractures versus diffusion-only in the rock that does not. Fracturing apparently diminishes the size of the diffusion-limited parts of the spheroidally weathering rock system to promote infiltration of meteoric fluids, therefore explaining the faster weathering advance rate in that rock.
Introduction

Pristine igneous bedrock does not usually contain enough water to support significant biomass. Once meteoric water infiltrates and reacts with the rock however, it begins to disaggregate into soil grains (Hochella and Banfield, 1995; Oguchi and Matsukura, 1999; White and Brantley, 2003; Meunier et al., 2007; Jin et al., 2011). This weathering process releases nutrients to solution and increases the porosity and surface area – all processes that enhance water retention to sustain ecosystem growth (Torn et al., 1997; Meunier et al., 2007; Graham et al., 2010). The initial growth of nanometer-scale porosity (here termed nanoporosity) is poorly understood (Montgomery and Brace, 1975; White et al., 1996; Putnis, 2002; Navarre-Sitchler et al., 2009). For example, although the health of terrestrial ecosystems relies on soil production, the rates of surface area growth during water infiltration into rock cannot yet be predicted because our fundamental understanding of the water-rock interface inside rocks is limited (Hochella et al., 1988). This limitation is one of the reasons we cannot accurately extrapolate laboratory reaction rates to the field in predictive numerical models (Navarre-Sitchler and Brantley, 2007; Navarre-Sitchler et al., 2011).

Traditionally, surface area is measured in Earth materials with sorption, Hg porosimetry, or microscopy (Ball et al., 1990; Rufe and Hochella, 1999; Brantley and Mellott, 2000; White and Brantley, 2003; Navarre-Sitchler and Brantley, 2007). However, sorption only characterizes accessible, connected pores, while microscopy only images extremely small subsamples (Fischer and Gaupp, 2004). Neutron scattering holds the promise of providing unique insights into how pores ranging in size from nm’s to 10s of μm’s in diameter develop during weathering of macroscopic rock volumes (Radlinski, 2006; Jin et al., 2011).

Here we probe how weathering creates surface area and porosity in two of the most common igneous rock compositions. The first sample, a basaltic andesite, is a hand sample-sized clast that weathers without fracturing (Sak et al., 2004). The second sample, a quartz diorite, is a 2 meter-sized corestone that weathers with spheroidal fracturing (Turner et al., 2003; Buss et al., 2008). In both cases, oxidation of iron-bearing minerals is the earliest weathering reaction but dissolution of plagioclase feldspar disaggregates the rock (Buss et al., 2008; Navarre-Sitchler et al., 2009; Navarre-Sitchler et al., 2011). The
plagioclase reaction front – i.e., the thickness of the zone across which plagioclase dissolves -- is 1-2 mm in the andesite but 40 cm in the granite. Furthermore, the weathering advance rate of the granite is nearly 3 orders of magnitude faster than the andesite despite the generally observed faster dissolution in the laboratory of calcium-rich plagioclase in the andesite relative to the more sodium-rich plagioclase in the granite (Bandstra et al., 2008). Here we use neutron scattering to understand differences in nanoporosity and surface area during the onset of weathering with and without spheroidal weathering in these rocks.

The weathering examples

The andesite clast (Figure 1a) was collected from a fluvial terrace in Costa Rica deposited ~125 ka in Costa Rica (Sak et al., 2004; Navarre-Sitchler et al., 2011). Clasts from these terraces range from basalt to andesite in composition (Navarre-Sitchler et al., 2011). The andesitic clast analyzed for this study was 61 weight % SiO$_2$ and 5 weight % (Na$_2$O + K$_2$O). The unaltered core of the clast contains ~67 volume % feldspar and ~27 volume % pyroxene. The core contains 1-3% porosity and abundant feldspar crystals (0.1-1 mm) in a matrix of small feldspar/pyroxene grains (1-10 µm) with trace ilmenite and magnetite (Sak et al., 2004; Navarre-Sitchler et al., 2009). The andesitic core is enveloped in a porous weathering rind (~ 50% porosity) of iron and aluminum oxides that is thought to have grown at a rate of 0.2 - 0.5 mm kyr$^{-1}$ (Sak et al., 2004; Pelt et al., 2008; Navarre-Sitchler et al., 2011). Feldspar and pyroxene dissolution at the rind-core interface was rate-limited by diffusion, occurring together over a reaction front thickness of ~ 1 mm (Table 1, Fig. 1B)(Navarre-Sitchler et al., 2011). The rind is friable and disaggregates easily once plagioclase is completely weathered (0.4 cm from the core).

The granitic rock, a quartz diorite dominated by crystals of plagioclase (~56%) in an interstitial matrix of submillimeter-sized quartz (~25%), was collected from the Luquillo rain forest in Puerto Rico (Figure 1C) (Murphy et al., 1998; White et al., 1998; Turner et al., 2003; Buss et al., 2008). Oxygenated waters infiltrate into meter-long vertical fractures into the granitic rock. Along the fracture surface, iron in biotite oxidizes (Buss et al., 2008). This reaction is inferred to cause volume expansion that results in spheroidal fractures spaced ~2.5 cm apart. Fractures wrap the central corestone like
onionskin (Fig. 1B). The intact but weathered rock layers between fractures are called rindlets (Buss et al., 2008). The zone of fracture-delineated rindlets around the central corestone is ~ 40 cm thick, i.e., starting at sample PR28 and grading into saprolite in the outer part above sample PR13 (Table 1, Fig. 1D). The spheroidal fractures anastomose and intersect to define rindlets that range in number from 13 to 16 around the corestone. Here, 10 rindlets along a vertical transect perpendicular to the corestone were sampled (Table 1, Fig. 1D). The outermost rindlets disaggregate easily.

3.0 Methods
3.1 Neutron Scattering Experiments

Neutrons penetrate through rock samples, scattering from interfaces between materials of different chemistry and density that define the scattering contrast. Scattered neutron intensity, measured as a function of scattering angle, can elucidate the internal structure of rocks at length scales from ~ 1 nm to 30 µm when both small angle (SANS) and ultra-small angle (USANS) neutron scattering experiments are performed. The scattering data provides statistical information about the topology and architecture of pore networks (Mildner et al., 1986; Radlinski, 2006; Anovitz et al., 2009; Jin et al., 2011; Navarre-Sitchler et al., in press). Through application of fractal and polydisperse hard-sphere models, the pore size distribution, pore volume, and internal interfacial area can be extracted from scattering data (Hinde, 2004; Radlinski, 2006).

Samples from each weathering system were prepared for small angle (SANS) and ultra small angle (USANS) neutron scattering experiments using standard thick section preparation. Each section was glued to a quartz slide and polished to a thickness of 150 µm to prevent multiple neutron scattering (Anovitz et al., 2009). For the andesite clast, one thick section was cut across the entire reaction front (Figure 1C). For the granitic system, individual sections were cut from rindlets at different distances from the core (Figure 1D). For the andesite, a cadmium (SANS) or gadolinium (USANS) mask with a 1.8 x 0.1 cm rectangular opening was used to define the area of analysis. The thick section was moved behind the stationary mask to measure scattering every 1 mm across the reaction front. For the rindlets, a cadmium mask with a 1.6 cm-diameter circular opening was used to define the area of analysis for both SANS and USANS.
Intensities, \( I(Q) \), of small-angle and ultra-small angle neutron scattering (SANS, USANS), were measured versus scattering vector, \( Q \), at the National Institute of Standards and Technology Center for Neutron Research (NCNR). SANS was measured using the NG7 beamline (Glinka et al., 1998) (\( \lambda = 8.09 \text{ Å} \) with a wavelength spread, \( \Delta\lambda/\lambda = 13\% \) ). Scattered neutrons were measured at sample-to-detector distances of 1.0, 4.0, and 15.3 m (the latter using biconcave MgF\(_2\) lenses) for a \( Q \) range of 8.9 x 10\(^{-4}\) to 4.3x10\(^{-1}\) Å\(^{-1}\), equivalent to spherical scatterers ranging in diameter from 15 to 7000 Å. Ultra-small angle neutron scattering (USANS) was measured at NCNR on the BT5 beamline (Barker et al., 2005) (\( \lambda = 2.38 \text{ Å} \) with \( \Delta\lambda/\lambda = 5.9\% \)) with a \( Q \) range of 4 x 10\(^{-5}\) to 3 x 10\(^{-3}\) Å\(^{-1}\). The overlap in SANS and USANS data allowed the two data sets to be merged.

Contrast-matching experiments were also performed for the andesitic basalt to assess connected versus unconnected porosity by saturating the thick section with a 75\% D\(_2\)O-H\(_2\)O mixture that had the same scattering length density (calculated as described in section 3.2 to be \( \sim 4.3\times10^{-6} \text{ Å}^2 \)) as the bulk unweathered rock. Samples were equilibrated with contrast-matched fluid for \( \geq 72 \text{ h} \). Scattering was measured from the contrast-matched samples in the same manner as described above.

### 3.2 Neutron scattering data analysis

Data were processed according to standard methods involving blank correction (a blocked beam and a quartz slide with Krazy Glue™), empty cell and background scattering correction, normalization, and conversion to absolute intensities. All SANS data reported here were observed to be azimuthally symmetric. Therefore the data were radially averaged and merged for the different \( Q \)-segments into one combined scattering curve. The normalized USANS data were de-smeared following protocols of NCNR (Kline, 2006). After de-smearing, data from USANS and SANS overlapped continuously across the \( Q \) range (Figure 2).

The de-smeared and combined dataset was then fit to equation 1 to determine the contribution of incoherent scattering from hydrogen to the intensity of scattered neutrons:

\[
I(Q) = bQ^{-m} + c .
\]  

(1)

This incoherent scattering (\( c \) in equation 1) was then subtracted from the data.
Neutrons passing through rocks with voids are scattered off interfaces between minerals and voids. The intensity of scattered neutrons is proportional to the volume of scattering objects (pores) and the scattering contrast ($\Delta \rho_j^*$) i.e. the difference in scattering length densities ($\rho_j^*$) of the rock phase and voids. The value of the coherent $\rho_j^*$ value for a single mineral phase is given by equation 2 (Rother et al., 2007):

$$\rho_j^* = \sum_{i=1}^{N} b_i \frac{\rho_j N_A}{M_j}, \quad (2)$$

Here, $b_i$ is the bound coherent scattering length of atom $i$ in phase $j$ and $N$ is the total number of atoms in phase $j$. $\rho_j$ is the mass density of mineral phase $j$, $M_j$ is the molar mass of phase $j$ and $N_A = 6.023 \times 10^{23}$ is Avogadro’s number. The summation is made over all atoms $i$ in the mineral. The values of the scattering length densities ($\rho_j^*$, Å$^{-2}$) calculated for minerals ranged from 3.94 - 4.85 x 10$^{-6}$ Å$^{-2}$ for the andesite and 3.5 - 4.52 x 10$^{-6}$ Å$^{-2}$ for the granite (Table 2). The value of $\rho_j^*$ was calculated from the bulk chemical formula of each rock composition normalized to one Si atom: 4.3x10$^{-6}$ Å$^{-2}$ for the unweathered andesite and 4.45 x 10$^{-6}$ Å$^{-2}$ for the unweathered granite (Table 2). While minerals within the samples have slightly different scattering length densities, scattering from the mineral–mineral boundaries is minimal compared to the large scattering contrast between minerals and unfilled voids characterized by $\rho_{\text{pore}}^* = 0$. Therefore, because pore–mineral interfaces scatter significantly but mineral–mineral boundaries do not, we followed published examples for NS for rocks and interpreted the samples using a two-phase approximation (Table 2) (e.g. Kahle et al., 2004; Radlinski, 2006; Anovitz et al., 2009).

Hinde (2004) summarizes a detailed discussion of the methodology of data fitting and analysis. In brief, using the two-phase approximation, the data were fit using routines in the program PRINSAS (Hinde, 2004). This fit was then used to calculate a pore size distribution and properties such as porosity and surface area.

Scattering data were plotted on Porod plots ($\log I(Q)^*Q^4$ vs. $\log Q$) to accentuate regions in $Q$-space described by different values of $m$ in equation (1) (Anovitz et al.,
2009). The data were assessed to determine where the Porod plots show linearity over ranges in $Q$ of at least one order of magnitude. Within each region of linearity, $\log I(Q)$ values were fit to $Q$ following Equation 3 to determine the slope $m$:

$$I(Q) = b Q^{-m}$$

3.4 BET surface area measurements

Surface areas were determined using Brunauer Emmett Taylor (BET) analysis with $N_2$ gas for two samples of andesite rind taken at 0.2 - 0.3 and > 0.4 cm from the core-rind interface. Sample size limitations prevented BET measurements on material taken from closer to the core or on samples spaced closer together across the reaction front. Isotherms were measured over a relative pressure range from $3 \times 10^{-5}$ to 1 using approximately 1.5 grams of sample using a Quantachrome Autosorb1. To enable BET measurement, the small samples had to be ground to particles of diameter ranging from 0.125 to 0.25 mm. The BET surface area is thus an upper limit to the actual BET surface area of the intact rind.

3.5 Transmission Electron Microscopy (TEM)

TEM images were collected from unweathered and weathered andesite and granite using a Hitachi HF-2000 cold-field-emission TEM, operated at 200kV accelerating voltage at the High-Temperature Materials Laboratory at Oak Ridge National Laboratory. Bright-field images (1024 x 1024 pixels) were recorded on a Gatan 794 multi-scan CCD camera system. The images of unweathered andesite were taken from the core while images of weathered andesite were collected from two points located approximately 2 or 5 mm from the core-rind boundary. TEM images of the unweathered and weathered granite were taken from samples PR03 and PR16, respectively (Fig. 1D). Sample PR03 is from the core while sample PR16 was 37 cm from the corestone-rindlet interface. Energy dispersive spectra (EDS) were collected for some spots using a Bruker EDS system.

4.0 Results and Discussion
4.1 Pore imaging

Pores were observed in the transmission electron microscope images at the same length scales probed by SANS. Many of these pores are located at grain boundaries and triple junctions in the unweathered samples (Figure 3, left-hand column of images). Dimensions of andesite pores imaged under TEM in the unweathered sample were generally <<1 μm but granite pores ranged from submicron- to micron-sized. In both compositions of unweathered protolith, some grain-grain interfacial angles at triple junctions are <60°, consistent with an interconnected pore network along the 3-grain boundaries (Lee et al., 1991).

In both samples, pores are more abundant and variable in size and shape after weathering (Figure 3, right-hand column of images). In the weathered granite, microfractures were commonly observed, especially near feldspar (Figure 3f,h). Microfractures often connected small pores (Figure 3f). Precipitates of kaolinite, sometimes covered by a layer of Mn-Fe oxyhydroxide, were also observed in micro-fractures (Fig. 3h). Microfractures were not observed in the andesite.

4.2 Porosity and surface area with weathering

SANS data for all samples were azimuthally symmetric and non-monotonous with respect to scattering angle, indicating randomly shaped and oriented features. The combination of SANS and USANS data provides information on features in the rocks of dimension or spacing, $d$, from 7 nm to ~30 μm ($d = 2\pi/Q$). Scattering intensities generally increased with distance from the unweathered rock especially for $d > ~75$ nm ($Q < 8x10^{-3}$ Å$^{-1}$, Figure 4a,b). The scattering increase is consistent with increasing porosity and surface area with increasing weathering.

Total porosity calculated from the SANS and USANS data (nanoporosity) increases in both weathering systems from < 3% in the unweathered cores to ~ 10% over the width of the reaction front for plagioclase dissolution (Table 1). In the andesite, where scattering was also measured with H$_2$O/D$_2$O, total porosity increases faster than connected porosity: 98% versus 83% of pores were connected before and after weathering, respectively (Figure 4a,c, Table 1). Surface areas calculated from NS increase from ~ 4 to 24 m$^2$ g$^{-1}$ in the andesite and ~2 to 13 m$^2$ g$^{-1}$ in the granite across the
plagioclase reaction front. For the andesite, the average SANS-calculated surface area of samples from 0.2 - 0.3 cm from the core equaled 11 m² g⁻¹. For comparison, surface area of the ground andesite measured by BET for roughly that location was 13 m² g⁻¹. The BET surface area increases to 30 m² g⁻¹ further out in the rind on another ground sample.

While the increases in porosity and surface area in the two weathering systems are similar, the evolution of the surface area and porosity with distance across the plagioclase reaction front is not. Porosity and surface area increase steadily over a distance of 4 mm across the plagioclase reaction front in the andesite (Figure 5). In contrast, despite plagioclase weathering in the rindlets, the specific surface area and porosity values derived from NS for the intact granite rindlets remain constant over ~35 cm of reaction front and only increase significantly in the last ~ 5 cm (Figure 5, 35-40 cm from the corestone).

In the center part of the granite rindlet zone, scatterers < ~20 nm were the only features in the network within the plagioclase reaction front where specific surface area increased consistently outward with distance from the core (Figure 6b). In the uppermost rindlet samples (PR15 and PR13) surface area increased for features < ~1000 nm. In contrast, the surface area in the andesite increased consistently for features < ~3000 nm once weathering initiated ~0.2 cm from the core-rind interface (Figure 6a and c).

Furthermore, initial connectivity in the unweathered andesite is only indicated for scatterers < 400 nm diameter, as shown in Figure 7 where scattering from H₂O-D₂O samples (filled symbols) are significantly less than from all pores, documenting that unconnected porosity is lower than total porosity. Pores observed at triple junctions in TEM images are in the size range of 100 to 200 nm (Figure 3c) and therefore may constitute the connected pore network in the unweathered andesite. The scattering that occurs from unconnected features > 400 nm in the unweathered andesite are presumed to be pores that are not preserved during preparation of the very tiny and thin TEM sections, explaining why large pores were not imaged by the TEM. During weathering of the andesite clast, the pore connectivity increases especially in pores > ~400 nm. After weathering, the specific surface area of all features in the andesite has increased, and little unconnected surface area remains (Figure 7).
Despite the lack of evidence of an increase in porosity and surface area from the SANS data across much of the granite rindlet zone (Figure 5b), weathering features were observed (Buss et al., 2008). Specifically, increasingly lower density and iron oxidation were both observed to document chemical weathering across the rindlet zone. Buss et al. (2008) and Fletcher et al. (2006) have suggested that oxygenated water infiltrates the rocks along fractures and that oxygen diffuses into the unfractured corestones and oxidizes ferrous minerals, perhaps driving the spheroidal fracturing itself (Fletcher et al., 2006). In general, reactive fluids are inferred to have infiltrated rindlets that are further from the corestone for longer durations. For example, the outer rindlets (PR13, PR15 and PR16) were exposed to reactive fluids for longer periods of time than those nearest the corestone. According to this conceptual model, the first reaction in each rindlet is diffusion inward of oxygen that drives oxidation of ferrous minerals such as biotite that can cause formation of both small and large fractures in the rock. This may explain why, unlike the andesite clast, the initial generation of porosity and surface area in the granite does not correlate with the extent of feldspar depletion (Table 1). The % feldspar in samples was calculated from the normalized concentration, i.e. the mass transfer coefficient $\tau$ (Anderson et al., 2002) using measured Na and Ti concentrations. These calculations have been described previously by Buss et al. (2008). For example, in rindlets PR15 and PR16, feldspar content is $\sim 97\%$ of the value in the original granite but porosity and surface area have increased 5- and 6-fold, respectively. The same amount of surface area and porosity increase in the andesite correlates with complete dissolution of the primary feldspar. This early development of porosity in the granite rindlets without total feldspar loss is attributed to the development of microcracks related to oxidation of biotite (Buss et al., 2008) but not related to wholesale dissolution. These ideas are further discussed in the context of the fractal nature of the rocks in the next section.

4.3 Fractal Dimensions

Scattering over several orders of magnitude in $Q$ that fits equation (3) yields a slope $m$ that defines either a surface ($4 < m < 3$) or mass fractal ($3 < m < 2$) (Radlinski, 2006). The fractal dimensions, calculated from $m$, vary from 2 to 3 for both surface and mass fractals and are defined as $D_s$ and $D_m$ respectively (equations 4a,b):
\[ D_s = 6 - m \]
\[ D_m = m \]  

(4a,b)

For a porous medium like a rock, the surface fractal dimension documents the roughness of the pore wall interface where \( D_s = 2 \) for smooth surfaces and 3 for extremely rough surfaces. Likewise, the mass fractal dimension provides insight into the self-affine character of the overall geometry of the pore volume, where \( D_m = 2 \) for monodisperse and 3 for polydisperse pore size distributions.

For example, to explain these concepts further, we can consider a Euclidean object such as a cube of size \( L \). For such an object, the area or mass varies with \( L^2 \) or \( L^3 \) respectively. In contrast, a surface fractal is a material whose surface area varies with \( L^{D_s} \) where \( D_s \) is not an integer. Likewise, for a mass fractal, the mass varies as \( L^{D_m} \) where \( D_m \) is not an integer (Radlinski, 2006). We discuss these ideas with respect to the two rock examples in the next sections.

4.3.1 Andesite

Scattering data across the plagioclase reaction front in the andesite fits equation 3 over two different portions of the data. These two fractal regions are defined by a break in slope at \( d \sim 1 \mu m \) for all sample points except in the outermost sample 0.4 cm from the core-rind interface where the plagioclase has weathered completely and the material is friable and is easy to disaggregate. For low \( Q \) (<6.5 x 10^{-4} \AA^{-1}, i.e. \( d = 1-24 \mu m \)), the slope \( m \) indicates mass fractal behavior, which is attributed here to scattering from pores (Table 1). The mass fractal dimension at low \( Q \) decreases across the reaction front (0 to 0.3 cm from core) from \(~2.9\) to \(2.6\) reflecting a shift in the pore size distribution with weathering from more polydisperse to more monodisperse (Figure 6). In contrast, at high \( Q \) (6.5 x 10^{-4} to 0.1 \AA^{-1}), slopes indicate a surface fractal that we attribute to scattering from bumps on pore-mineral interfaces at length scales from \( d = 6 \) nm to 1 \mu m (Table 1). The surface fractal dimension also decreases with weathering from \(~2.7\) or \(2.8\) in the core to \(2.5\) at 0.3 cm from the core. This decrease in surface fractal dimension is consistent with smoothing of mineral surfaces during weathering of the andesite. Like the increase in porosity and surface area (Fig. 5), the evolution of fractal dimensions
across the reaction front are generally consistent with gradual changes in the pore network until 0.4 cm from the core.

A calculated increase in specific surface area can result either from increased roughness of surfaces or increased porosity (or both). The decrease in surface fractal dimension with distance from the unweathered core is most consistent with weathering resulting in smoother surfaces. Therefore, the increase in specific surface area during weathering of the andesite is attributed largely to increased porosity.

In the outermost andesite rind sample, a non-linear region was identified at high $Q$ and no slope was determined. In contrast, the mass fractal dimension for that sample determined from the low $Q$ data is 2.95. This value, close to 3, and the non-linear behavior is indicative of a very irregular pore network in the rind that does not exhibit self-similarity. Overall, the changes in mass and surface fractals across the rind are inferred to document the increasing disaggregation of the sample as plagioclase weathers: once disaggregation reaches significant extent, scattering no longer fits equation (3) at high $Q$, but the non-disaggregated material still retains a pore geometry best described with a mass fractal close to 3.

### 4.3.2 Granitic rock

Similar to the andesite, the unweathered granite was fit with a mass fractal at low $Q$ ($D_m \sim 2.8$) and a surface fractal at high $Q$ ($D_s \sim 2.5$). The break in slope occurred at $d \sim 650 \text{ nm}$ (Fig. 4d). Across the rindlet zone, however, three fractal regions were identified and, for all but the inner-most rindlet, all three of these regions are indicative of surface fractal behavior (Table 1). The surface fractal dimension of the high $Q$ data shows a tendency to increase across the rindlet zone from $\sim 2.4$ to $2.7$ consistent with increased surface roughness at small length scales with weathering. A region at mid-$Q$ was fit with a surface fractal dimension of $2.2$ to $2.3$. These relatively smooth surfaces at length scales $\sim 60$ to $600 \text{ nm}$ are most consistent with microcracks observed in TEM images. Finally, the low $Q$ data for the rindlets are described by a surface fractal that varies in dimension from $2.7$ to $2.8$.

At the point where the rindlet zone transitions to saprolite (PR15 (38 cm) and PR13 (40 cm)), the fractal behavior changes abruptly. PR15 is described by a surface
fractal dimension at low $Q$ with $D_s = 2.9$ but this sample has a non-linear (non-fractal) region at high $Q$. In contrast, PR13 (40 cm) exhibits surface fractal behavior with $D_s = 2.3$ at high $Q$ and non-fractal behavior at low $Q$. Thus, scattering from these more disaggregated samples is inconsistent and difficult to interpret and is likely related to the process of disaggregation.

Unlike the andesite, abrupt changes in fractal behavior in the granite were identified across the plagioclase reaction zone (rindlet zone). These changes in the fractal behavior across the rindlet zone demonstrate changes to the pore network that do not correlate to feldspar depletion, porosity, or surface area (Table 1 and Figure 5b).

5.0 Mechanisms of weathering

Navarre-Sitchler et al. (2009, 2011) have shown ample evidence that the dominant mechanism of transport of reactants and products during weathering of the andesite clast is diffusion. Apparently, in the absence of fracturing, diffusion-controlled weathering dominates producing relatively smooth changes in porosity, surface area and fractal behavior across the mm-wide reaction front (Table 1, Fig. 5a). Throughout almost the entirety of weathering of this andesitic clast, the material was best characterized as both a mass and a surface fractal.

In contrast, the granite weathering system is best classified as transforming from a mass fractal to a surface fractal across the plagioclase reaction front. Apparently, the fracturing of this sample causes relatively abrupt changes across the 10’s of cm wide reaction front. These changes coincide with the onset of fracturing (PR 28) and advanced chemical weathering and disaggregation (PR13 and PR15). Based on petrographic observation (Buss et al., 2008), each of the rindlets is akin to a separate weathering system where a reaction front develops between the fracture and the unweathered diffusion-limited core of the rindlet, experiencing inward diffusion of reactants, not unlike the andesitic clast. However, the rindlets also experience further micro-cracking, reducing the size of the diffusion-limited part of the weathering rindlet rock further. In the zones between micro-fractures, the overall mechanism of chemical weathering is inferred to be the same in both systems (diffusion-limited mineral dissolution) – however, the micro-fracturing in the granite breaks up the original granite corestone into even
smaller diffusion-limited weathering subregions as weathering progresses across the rindlet zone. Fracturing accelerates the weathering by forming rindlets, but further (micro)fracturing accelerates the weathering even beyond that – and the microfracturing could even explain why the weathering advance rate in the granite is nearly 3 orders of magnitude faster than that of the andesite (Fletcher et al., 2006; Pelt et al., 2008). This acceleration of weathering is particularly noteworthy given that dissolution of Ca-rich plagioclase measured in the laboratory for andesite is generally faster than that measured for the Na-rich plagioclase in the granite (Bandstra et al. (2008), and references therein).

The accelerated rate of weathering of the granite may also be affected by a bacterial ecosystem that has been observed at the bedrock-saprolite interface in that system (Buss et al., 2005; Minyard, et al., 2011; Bruns, et al., in press). Putatively, this ecosystem is supported by Fe-oxidizing primary producers. Beyond identification of bacterial cells and species, mobilization of Fe(II)_{aq} and changes in Fe isotopic signatures have also been identified at this interface, consistent with bacterial inputs of protons and organic ligands (Buss et al., 2010). Fe + Mn precipitates have also been identified in the outer rindlets (see for example, the Fe-Mn precipitate shown in Fig. 3h). Such precipitates, not observed in the innermost rinds, document downward infiltration of organic-rich, acidic, Fe,Mn-charged fluids into the spheroidally weathering rock. All of these lines of evidence are consistent with infiltration of advecting meteoric fluids into the rindlet zone.

**Conclusions**

Neutron scattering was used to measure changes in nano-porosity and surface area associated with initial weathering of low porosity, igneous rocks. Before weathering, the pore networks of both rocks are described by mass and surface fractals. Furthermore, the transition between mass and surface fractal behavior in both rocks occurs for scattering features of dimension $d \sim 1 \mu m$.

One of the rocks (the basaltic andesite) dissolves without spheroidal weathering: in that clast, the dominant mechanism of transport is diffusion. During diffusive weathering of that andesite, porosity and surface area increase relatively smoothly across the mm-thick reaction front of plagioclase dissolution. The mass and surface fractal
behavior is mostly retained until rind disaggregation, but the fractal dimensions decrease with weathering. These changes are consistent with increasing connectivity of pores without significant roughening of the pore surfaces. Lack of roughening during dissolution of crystalline surfaces is consistent with dissolution close to equilibrium, a feature consistent with transport limitation.

The second rock is a spheroidally weathered quartz diorite which shows evidence for both chemical reactions and fracturing across the 40 cm-thick reaction zone for plagioclase. The reaction front consists of 2.5-cm thick rindlets subtended by spheroidal fractures that wrap the granitic corestone like onionskin. In addition to the rindlet-defining fractures, the rindlets themselves are criss-crossed by micro-fractures imaged in optical and electron microscopy. Across this zone of micro-fractured rindlets, the rock transforms from a mass + surface fractal into three surface fractals. In the rindlets, the specific surface area and porosity determined from NS does not increase significantly until disaggregation begins. The transformation of the corestone from a mass + surface fractal to several surface fractals, the increase in the surface fractal dimension measured at high $Q$ during weathering, and the observation of precipitated Fe and Mn in some rindlets are all taken together as evidence that the transport mechanism for reactants and products in this weathering rock is advective infiltration + diffusion rather than just diffusion. Nonetheless, it is inferred that the diffusion-limited weathering subzones within the rindlets are somewhat similar to the plagioclase reaction zone in the andesite.

Thus, the spheroidal weathering in the granite leads to advective infiltration into the fractures and increased interfacial area where diffusion-limited weathering can occur. In contrast, weathering in the non-fractured andesite is diffusion-limited across a single interface, the core-rind boundary. The fracturing translates to a faster weathering advance rate in the granite compared to the andesite. All of these observations yield a more mechanistic picture of how porosity opens up inside igneous rocks during weathering, leading to solubilization of nutrients and storage of water that can nurture and grow terrestrial ecosystems.

**Acknowledgements.** SLB acknowledges NSF CHE-0431328 and DOE DE-FG02-05ER15675; DRC acknowledges support from the Basic Energy Sciences Energy Frontier Research Center “Nanoscale Control of Geologic $\text{CO}_2$”. GR acknowledges
support from the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy. Oak Ridge National Laboratory is managed by UT-Battelle, LLC for the U.S. Department of Energy under Contract DE-AC05-00OR22725. D. Mildner, A. Jackson and the National Institute of Standards and Technology, U.S. Department of Commerce, are acknowledged for neutron beam support and facilities. Anonymous reviewers are acknowledged for their thoughtful and very helpful comments on an earlier version of this manuscript. H. Buss acknowledges support from the Luquillo Critical Zone Observatory and funding from NSF EAR-0722476 to F. Scatena (Univ. of Pennsylvania).

References:


Navarre-Sitchler, A., Mouzakis, K., Rother, G., Dewers, T.A., Heath, J., McCray, J.E., in press. Nano- to micro-meter scale characterization of pore networks in fine-
grained rocks using electron microscopy and small angle neutron scattering. Microscopy and Microanalysis.


## Table 1. Results from neutron scattering analysis

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<td>I.D.</td>
<td>Distance (cm)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Density (g/cm&lt;sup&gt;3&lt;/sup&gt;)</td>
<td>Total porosity (%)&lt;sup&gt;b&lt;/sup&gt; (connected)</td>
<td>D&lt;sup&gt;d&lt;/sup&gt; @ low Q</td>
<td>D&lt;sup&gt;d&lt;/sup&gt; @ mid Q</td>
<td>D&lt;sup&gt;d&lt;/sup&gt; @ high Q</td>
<td>%&lt;sup&gt;c&lt;/sup&gt; of parent feldspar</td>
<td>Total surface area (m&lt;sup&gt;2&lt;/sup&gt;/g)&lt;sup&gt;b&lt;/sup&gt; (connected)</td>
<td>BET surf. Area (m&lt;sup&gt;2&lt;/sup&gt;/g)</td>
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<td>2.74 ± 0.03</td>
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<td>0</td>
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<td>100</td>
<td>1.3</td>
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</table>

<sup>a</sup>Distance from the pristine unweathered rock (= zero).

<sup>b</sup>Porosity and surface area as determined from scattering data as described in text. Values in parentheses are connected porosity or surface area as measured for andesite samples, granite samples were not analyzed for unconnected porosity. nm = not measured

<sup>c</sup>Surface fractals are marked by †, all others are mass fractals.

<sup>d</sup>A separate mid-Q region with distinct slope was observed in some of the granite samples.

<sup>e</sup>Calculated from the mass transfer coefficient τ (Anderson et al., 2002) using measured Na and Ti concentrations.

nm= not measured.
Table 2. Calculated scattering length density ($\rho_j^\circ$) for rock minerals

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Formula</th>
<th>Density g cm$^{-3}$</th>
<th>$\rho_j^\circ$ Å$^{-1}$</th>
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</thead>
<tbody>
<tr>
<td>Andesite Plagioclase</td>
<td>Na$<em>{0.387}$Ca$</em>{0.613}$Al$<em>{1.613}$Si$</em>{2.387}$O$_8$</td>
<td>2.69</td>
<td>3.94 x 10$^4$</td>
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<tr>
<td>Granite Plagioclase</td>
<td>Na$<em>{0.50}$Ca$</em>{0.48}$K$<em>{0.01}$Al$</em>{1.43}$Si$_{2.56}$O$_8$</td>
<td>2.65</td>
<td>4.18 x 10$^4$</td>
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<tr>
<td>Andesite Augite</td>
<td>Ca$<em>{3.3}$Mg$</em>{0.23}$Si$_{3.3}$O$_3$</td>
<td>3.3</td>
<td>4.85 x 10$^4$</td>
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<tr>
<td>Plagioclase</td>
<td>SiO$_2$</td>
<td>2.69</td>
<td>4.22 x 10$^4$</td>
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<tr>
<td>Andesite Hornblende</td>
<td>Ca$<em>{2.6}$Na$</em>{0.29}$K$<em>{0.06}$Mg$</em>{0.02}$Fe$<em>{0.04}$Al$</em>{0.42}$SiO$_2.88$</td>
<td>4.3</td>
<td>4.52 x 10$^4$</td>
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<tr>
<td>Granite Hornblende</td>
<td>K$<em>{1.73}$Na$</em>{0.29}$K$<em>{0.06}$Mg$</em>{0.02}$Fe$<em>{0.04}$Al$</em>{0.42}$SiO$_2.88$</td>
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<td>4.52 x 10$^4$</td>
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<tr>
<td>Biotite</td>
<td>K$<em>{0.89}$Fe$</em>{1.28}$Mg$<em>{1.19}$Mn$</em>{0.02}$Ti$<em>{0.18}$Al$</em>{0.16}$Si$<em>{2.88}$Al$</em>{1.12}$O$_{10}$(OH)$_2$</td>
<td>3.1</td>
<td>3.50 x 10$^4$</td>
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<tr>
<td>Ilmenite</td>
<td>Fe$_2$TiO$_3$</td>
<td>4.79</td>
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Normalized rock formulas:

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<th>Minerals</th>
<th>Formula</th>
<th>Density g cm$^{-3}$</th>
<th>$\rho_j^\circ$ Å$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Andesite</td>
<td>Na$<em>{0.14}$K$</em>{0.06}$Ca$<em>{0.08}$Mg$</em>{0.02}$Fe$<em>{0.04}$Al$</em>{0.42}$SiO$_2.88$</td>
<td>2.7</td>
<td>4.3 x 10$^4$</td>
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<tr>
<td>Granite</td>
<td>Na$<em>{0.1}$K$</em>{0.02}$Ca$<em>{0.1}$Mg$</em>{0.06}$Fe$<em>{0.09}$Ti$</em>{0.01}$Al$_{0.36}$SiO$_2.95$</td>
<td>2.6</td>
<td>4.45 x 10$^4$</td>
</tr>
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</table>
Figure 1. A) Weathered andesite clast from Costa Rica. Orange/brown rind is about 2.9 cm thick in this image. B) A thick section was cut across the weathering interface for neutron scattering analysis. A mask with a 1 mm rectangle cut-out was used to define the area of impingement of neutrons with the sample. This mask was placed over the thick section so that the cutout was parallel with the reaction front (transition from grey to orange) and was moved in 1 mm increments between data collection. C) Roadcut showing spheroidally weathered granite corestone in Puerto Rico. Corestone is center grey part and darker grey rindlets envelop the corestone. Thickness of the rindlet set was about 40 cm in the upper part where sampled. D) Diagram showing sample locations: parent samples (hachured, samples PR35, PR03) and rindlet samples (collected from individual rindlets as shown by labels). The rindlet zone begins to transition to saprolite at sample PR15 and PR13. All samples were cut into thick sections for neutron scattering.
Figure 2. SANS (closed circles) and de-smeared USANS (open circles) data overlap and are well connected across $Q$ values for the unweathered basaltic andesite (A) and granitic rock (B). Incoherent scattering from hydrogen in the samples produces the constant intensity values at high $Q$ in both samples.
Figure 3. TEM micrographs of unweathered (left) and weathered (right) andesite (top) and quartz diorite (bottom). In both unweathered rocks (a, g), pores at triple junctions show contact angles < 60°, consistent with interconnected tubules of cross-section < 1 μm (Lee et al., 1991). Unconnected pores < 0.5 μm diameter also decorate grain boundaries (c, e). In the weathered samples, pores show more variable shapes and sizes (b, e: light grey areas are pores). Microcracking was also observed in the granitic example: fractures connect pores especially in feldspar-rich zones (f). Fracturing is attributed to oxidation of ferrous minerals (Buss et al., 2008). Only kaolinite precipitates were observed in micro-fractures in early rindlets close to the corestone. In outer rindlets, Mn-Fe oxide coatings were also observed. Equant crystallites of kaolinite growing in a micro-fracture in plagioclase from an outer rindlet are shown in (h) with a coating of a dark Mn-Fe phase.
Figure 4. Scattering plots for total porosity (open symbols) in unweathered (squares) and weathered (circles) andesite (A) and granite (B). The weathered samples were measured 0.4 mm from rind-core interface (andesite) or 40 cm above the corestone (granite). For unweathered (A) and weathered (C) zones of the andesite sample, contrast matching delineated scattering due to unconnected (filled symbols) and total porosity (open symbols). More than 80% of total porosity is connected. The connected porosity is 1.5% and 5.5% of the total rock volume in the unweathered and weathered andesite samples, respectively. Only samples in the granitic rindlet zone (PR25, stars, multiplied by 0.1 for plotting purposes) show three regions of fractal scattering, indicated by line fits (D). In contrast, unweathered (PRO3, data multiplied by 0.001 for plotting purposes) and weathered (PR13) granite samples show two regions of fractal scattering.
Figure 5. Total porosity (closed squares) or specific surface area (open circles) for andesite that weathers without fracturing (a) and granite that weathers with fracturing (b) plotted versus distance from protolith (Table 1). The rindlet zone in (b) lies between 6 and 37 cm. Total porosity and specific surface area are calculated using PRINSAS. This surface area does not include the contributions from pores with radius larger than ~ 30 microns. Specific surface area varies in parallel with porosity in the granite (b) where porosity is described by surface fractals but not in the andesite (a) where porosity is described as a mass and a surface fractal.
Figure 6. Specific surface area (SSA) plotted versus scatterer diameter $d$ for andesite (A) and granite (B) and logarithm of SSA plotted versus $d$ for andesite (C) and granite (D). Weathered samples, shown in circles, document generally increasing SSA with increasing weathering. Samples from the plagioclase reaction front in andesite and granite rindlet zone are stars; unweathered samples are shown as squares. Closed symbols in C are calculated from scattering in presence of $D_2O/H_2O$: i.e., surface area calculated for scatterers that are unconnected under contrast matching conditions (see text). Total SSA increases with weathering more for smaller scatterers than for larger scatterers in both andesite and granite (A and B). (C) Plot of log specific surface area versus diameter shows increased surface area with weathering in the andesite across the entire length-scale of scatterers interrogated. (D) Plot of log SSA versus diameter emphasizes that micro-fracturing observed in rindlet sample PR25 (stars) especially increases SSA calculated for scattering features that are smaller than 0.01 μm in the the granitic material.
Figure 7. In unweathered andesite only pores of diameter $< \sim 400$ nm are connected (arrow A delineates the difference between unconnected and connected in unweathered andesite). Andesite weathering connects the larger pores (arrow B delineates the change from unweathered and unconnected to weathered and connected).