

Supplemental Material Item S1: Supplemental Text “Anisovolumetric weathering in granitic saprolite controlled by climate and erosion rates”

Clifford S. Riebe^{1*}, Russell P. Callahan¹, Sarah B.-M. Granke¹, Bradley J. Carr¹, Jordan L. Hayes², Marlie S. Schell¹ and Leonard S. Sklar³

¹Department of Geology and Geophysics, University of Wyoming, Laramie, Wyoming 82071, USA

²Department of Earth Sciences, Dickinson College, Carlisle, Pennsylvania 17013, USA

³Department of Geography, Planning and Environment, Concordia University, Montréal, Quebec H3G 1M8, Canada

*e-mail: criebe@uwyo.edu

Saprolite sampling methods

We sampled weathered regolith from the subsurface using a Geoprobe 7822DT direct push system during July 2019 at two sites: Fine Gold and Soaproot (see Figure 1, main text). All but a few of the cores were collected in 3.2 cm diameter tubes, with the rest collected in 4.3 cm diameter tubes. Each tube was set snugly within in a metal Geoprobe sleeve (matched in diameter to the tube we chose). Using hydraulic pressure from the Geoprobe, we pushed the sleeve vertically exactly 52 cm into the subsurface and used an extension system for each successive (i.e., each deeper) 52 cm push. This samples the subsurface in a manner analogous to standard drive-cylinder methods for sampling soils at the surface (e.g., ASTM designation D2937-17), differing in practice mainly in the need to use an extension system to sample regolith from depths below the top 0.52 m.

The cross-sectional area of the tube times the 52 cm length of push equals the volume of regolith sampled in each push. Hence, by measuring the mass of material contained within the tube, we were able to quantify bulk density and thus estimate porosity for the depth interval spanned by each push. Any compaction of the saprolite that occurred during each push (e.g., due to shear stresses along tube sidewalls) would not affect our analysis of bulk density, because the volume is based on push length, not length of core recovered.

Soils were typically less than 1-m thick, so the first or second push was generally sufficient to reach the depth of the soil-saprolite transition, which was often detectable in a change of engine load on the Geoprobe when transitioning from soil, which offered little resistance, to saprolite, which required increased pressure. This depth generally matched visual evidence from the cores of a sharp drop in organic matter at the top of saprolite.

Although organic matter was not as abundant in saprolite as it was in soil, there was some evidence of roots at depth in saprolite at the Soaproot site. For example, during some of the 0.52 m pushes, including several pushes close to the surface, resistance to pushing dropped abruptly, which we interpreted to reflect the presence of macropores likely created by largely empty root casts. In addition, roots were occasionally cut and retained and observed in the cores we analyzed. This provides further support for the idea that rooting contributes to porosity production via strain in saprolite (see main text) and thus corroborates the central finding of anisovolumetric weathering in saprolite.

To the extent that some of the material in the cores was organic and thus not derived from weathered rock, it would imply that the mass of weathered protolith was even lower over the depth interval in question than we measured in the lab. Hence, to the extent that organic matter was present in the cores, it caused us to overestimate the mass of weathered protolith and thus underestimate the porosity produced by strain of protolith. It can therefore be reasoned that the presence of roots in the cores would cause us to underestimate, not overestimate strain, implying that our conclusions about anisovolumetric weathering are conservative with respect to the presence of organic matter.

Low-density roots in the cores also help explain how the subsurface can retain its structure, despite the very high porosity implied by measurements from some of our samples, and in particular the three near-surface samples with >70% porosity at Soaproot. Roots open up space between minerals in

rock and fill voids thus cause strain without adding much mass. Hence, in addition to causing substantial strain of saprolite, roots can also provide structural support to the subsurface despite the high porosity that they helped produce. In any case, the high values of porosity and thus strain are consistent with the highly weathered, spongiform material we extracted from depth intervals that had the highest values.

In summary, there are a number of reasons why we are confident in accuracy of our porosity measurements. First, our methods are similar to ASTM push coring methods used for measuring soil density at the surface. Additionally, we were able to verify, after each push of 0.5 m, the retention of 100% of the distance pushed; if material was lost during extraction of a sample tube, the next tube would not sit flush to the coring device. Retention was aided by core catchers installed in each of the tubes. When some sample is nonetheless lost during extraction (and this never happened at the Soaproot or Fine Gold sites reported on in the main text), these losses are also obvious in the tube itself. Finally, to the extent that our samples included organic matter, in addition to weathered rock, it would cause us to overestimate the bulk density of the weathered rock and thus underestimate porosity produced by strain in the subsurface. Hence, our estimates of strain likely are minimum estimates of strain, particularly at the middle elevation (Soaproot) site, where organic material was more common.

Derivation of mass balance formulations

By definition, strain (ε) is the change in volume (V) expressed as a fraction of the initial volume.

$$\varepsilon = \frac{V_w - V_p}{V_p} = \frac{V_w}{V_p} - 1 \quad (\text{S1})$$

Here and elsewhere in the text, the subscripts p and w refer to protolith (i.e., the initial state) and weathered saprolite and soil. Volume is defined in terms of mass (M), density (ρ), and porosity (ϕ) for both protolith and weathered material according to Eq. S2.

$$V_p = \frac{M_p}{\rho_{g,p}(1 - \phi_p)} \quad (\text{S2a})$$

$$V_w = \frac{M_w}{\rho_{g,w}(1 - \phi_w)} \quad (\text{S2b})$$

The subscript g in the density term indicates that it is a mineral grain density of the material. (The porosity terms are needed because these expressions use mineral grain density rather than bulk density.)

Following previous derivations (Brimhall and Dietrich, 1987), we combine Eqs. S1 and S2 and obtain Eq. S3, which shows how porosity in weathered saprolite or soil is related to changes in mass, volume, and density as protolith is converted to weathered material.

$$\phi_w = 1 - \frac{V_p}{V_w} \frac{\rho_{g,p}}{\rho_{g,w}} \frac{M_w}{M_p} (1 - \phi_p) \quad (\text{S3})$$

Although the derivation of Eq. S3 is conceptually simple, the equation is impractical to solve, because the relevant protolith of a weathered soil or saprolite no longer exists, making its initial mass and volume impossible to directly measure. However, geochemists have developed approaches for indirectly quantifying volumetric strain and mass loss of individual elements using the bulk geochemistry of weathered saprolite and unweathered proxies for protolith.

Mass-transfer coefficients. The chemical mass loss of a soluble element from soil or saprolite can be expressed as its mass-transfer coefficient ($\tau_{i,j}$), which relates changes in concentration (C) of the

soluble element (subscript j) to the enrichment of an immobile element or mineral (subscript i) in weathered material relative to protolith (Brimhall and Dietrich, 1987).

$$\tau_{i,j} = \frac{C_{j,w}M_w}{C_{j,p}M_p} - 1 = \frac{C_{j,w}C_{i,p}}{C_{j,p}C_{i,w}} - 1 \quad (\text{S4})$$

The central terms of Eq. S4 show that $\tau_{i,j}$ is the fractional mass loss of the element relative to its mass in the protolith. When the immobile element is highly enriched or when the soluble element is highly depleted, $\tau_{i,j}$ approaches -1 , implying that all the element's mass in the protolith has been lost due to chemical weathering. Conversely, when none of the element's mass has been lost, $\tau_{i,j}$ approaches 0, because there is little or no enrichment of the immobile element in the weathered material and little or no depletion of the soluble element. The mass-balance-derived formula in Eq. S4 shows that chemical losses from weathered material can be estimated using bulk geochemical data from protolith and weathered material. Because Zr, Ti, and Nb are generally present in relatively insoluble minerals, they are commonly used as immobile reference elements in Eq. S4 to infer mass losses of individual elements from weathered material.

The bulk mass-transfer coefficient or “bulk tau”. Although $\tau_{i,j}$ has been highly informative over the years about mass losses in saprolite and soil, it only provides an element-by-element perspective that does not integrate the overall mass loss in weathered material. Thus, it may not fully capture the contribution of mass loss to total porosity, particularly when applied to elements that have low abundance in the protolith.

To quantify how mass loss influences porosity, we use the bulk tau (τ), which is equal to the sum over all n elements (both mobile and relatively immobile) of mass loss weighted by each element's concentration in the protolith (Ague, 1991; Hayes et al., 2019).

$$\tau = \sum_{j=1}^n C_{j,p}\tau_{i,j} = C_{1,p}\tau_{i,1} + C_{2,p}\tau_{i,2} + \dots + C_{n,p}\tau_{i,n} \quad (\text{S5})$$

Using Eq. S4 to expand terms in Eq. S5 yields Eq. S6a, which can be simplified as shown in Eq. S6b.

$$\tau = (C_{1,w}\frac{C_{i,p}}{C_{i,w}} - C_{1,p}) + (C_{2,w}\frac{C_{i,p}}{C_{i,w}} - C_{2,p}) + \dots + (C_{n,w}\frac{C_{i,p}}{C_{i,w}} - C_{n,p}) \quad (\text{S6a})$$

$$\tau = (\frac{C_{i,p}}{C_{i,w}})(C_{1,w} + C_{2,w} + \dots + C_{n,w}) - (C_{1,p} + C_{2,p} + \dots + C_{n,p}) \quad (\text{S6b})$$

The sum of all element concentrations in the weathered material $C_{1,w} + C_{2,w} + \dots + C_{n,w}$ equals one, and likewise the sum of all element concentrations in protolith $C_{1,p} + C_{2,p} + \dots + C_{n,p}$ equals one. Therefore, Eq. S6b reduces to Eq. S7.

$$\tau = \frac{C_{i,p}}{C_{i,w}} - 1 \quad (\text{S7})$$

Thus, τ can be readily estimated from measurements of immobile element concentrations in protolith and weathered material. Crucially, it integrates across the mass losses in all the individual elements (Eq. S5). As shown later, it also provides an overall assessment of the contribution of mass loss to changes in saprolite porosity.

Volumetric strain. Because the protolith that created a weathered sample is no longer present, it is impossible to measure the initial protolith volume and solve for strain using Eq. S1. Fortunately, strain, like τ , can be expressed in terms of changes in immobile element concentration as bedrock is exhumed to the surface. For immobile elements, mass losses are negligible, so an immobile element's mass in the protolith should equal its mass in the weathered material, as shown in Eq. S8.

$$V_w \rho_{b,w} C_{i,w} = V_p \rho_{b,p} C_{i,p} \quad (\text{S8})$$

Here, the subscript b indicates bulk, rather than a mineral-grain density. Following previous derivations (Brimhall and Dietrich, 1987), we combine Eqs. S1 and S8 to obtain Eq. S9.

$$\varepsilon = \frac{V_w}{V_p} - 1 = \frac{\rho_{b,p} C_{i,p}}{\rho_{b,w} C_{i,w}} - 1 \quad (\text{S9})$$

Thus, strain can be estimated from measurements of bulk density and bulk geochemistry from samples of protolith and weathered soil. Positive strain indicates dilation, and negative strain indicates contraction; a strain of 1 (i.e., 100%) implies a doubling in protolith volume during weathering. However, because strain is conventionally assumed to be negligible in saprolite (see main text), and because bulk density is not often measured in soil profiles, strain has rarely been quantified in weathering studies.

Relationships between mass loss, strain, and porosity. Using substitution, we can reframe Eq. S3 in terms of bulk tau (Eq. S7) and strain (Eq. S9) instead of mass, volume, and density. This yields Eq. S10 (i.e., Equation 1 in the main text).

$$\phi_w = 1 - \frac{\tau + 1}{\varepsilon + 1} (1 - \phi_p) \quad (\text{S10})$$

Eq. S10 assumes that the average mineral grain density of the weathered material is equal to the average mineral grain density of the protolith. To the extent that weathering preferentially produces minerals with density less than minerals in protolith, Eq. S10 will tend to underestimate porosity. However, many secondary minerals differ by only a few percent in density from their parent minerals (cf. feldspar and kaolinite), so this bias should be small compared to the creation of porosity by strain and mass loss (which are both accounted for in Eq. S10). Hence, Eq. S10 shows that porosity can be inferred if the total strain and mass loss are both known.

The fraction of porosity produced by chemical and physical weathering. A chemical mass loss that occurs during weathering produces an effective loss of protolith volume—and a commensurate opening of voids—equal to the mass loss divided by the density of the protolith. Hence, the production of porosity (i.e., the gain in fractional volume of voids, relative to the protolith) associated with the chemical mass loss is equal to the fractional mass loss (which is equal to negative τ , as shown in Eq. S7). Therefore, when $\phi_p = 0$, the fraction of porosity produced by chemical mass loss, F_{PC} , is equal to $-\tau/\phi_w$.

$$F_{PC} = \frac{-\tau}{\phi_w} = \frac{-\tau}{1 - \frac{\tau+1}{\varepsilon+1}} = \frac{-\tau(\varepsilon+1)}{\varepsilon-\tau} \quad (\text{S11})$$

The fraction of porosity produced by strain, F_{PP} , is equal to the complement of F_{PC} .

$$F_{PP} = 1 - F_{PC} = 1 - \frac{-\tau(\varepsilon+1)}{\varepsilon-\tau} = \frac{\varepsilon(\tau+1)}{\varepsilon-\tau} \quad (\text{S12})$$

Multiple linear regression analysis

We used a multiple linear regression model to predict F_{PP} from erosion rate (ER) and average annual precipitation (AAP), two variables that have been used with success to explain variance in previous studies of weathering rates (Riebe et al., 2004). Recognizing the obvious nonlinearity between F_{PP} and AAP in the dataset during initial exploratory analysis, we use the base ten logarithm of AAP to linearize it for our regression analysis. Hence the regression model takes the form shown in Equation S13.

$$F_{PP} = a + b \times ER + c \times \log_{10} AAP \quad (\text{S13})$$

Here a , b , and c are best-fit parameters in the multiple linear regression. We centered the data to ensure that we obtained an unbiased estimator of the uncertainty and p value of the regression intercept a . That is, we subtracted the mean erosion rate from the measured erosion rates and also subtracted the mean of the base ten logs of average annual precipitation from the base ten logs of the average annual precipitation rates before performing the regression. However, we report a in Table S1 as the value associated with $ER = 0$ and $\log_{10}(AAP) = 0$ (i.e., the uncentered intercept).

Table S1. Multiple linear regression parameters and uncertainties

Parameter (units)	Estimate	Standard error	p value
a (unitless)	2.57	0.026	0.0001
b (y/mm)	5.1	1.5	0.026
c ($1/\log_{10}(\text{mm/y})$)	-0.74	0.10	0.0016

The overall coefficient of multiple determination R^2 was 0.94, indicating that variations in erosion rate and annual average precipitation explain 94% of the variance in F_{PP} across the sites. The p value for the regression model, the erosion rate parameter (b), and the $\log_{10}(AAP)$ parameter (c) were 0.0035, 0.026, and 0.0016, respectively (Table S1).

References

- Ague, J.J., 1991, Evidence for major mass transfer and volume strain during regional metamorphism of pelites: *Geology*, v. 19, p. 855–858, doi:10.1130/0091-7613(1991)019<0855:EFMMTA>2.3.CO;2.
- Brimhall, G.H., and Dietrich, W.E., 1987, Constitutive mass balance relations between chemical composition, volume, density, porosity, and strain in metasomatic hydrochemical systems: Results on weathering and pedogenesis: *Geochimica et Cosmochimica Acta*, v. 51, p. 567–587, doi:10.1016/0016-7037(87)90070-6.
- Hayes, J.L., Riebe, C.S., Holbrook, W.S., Flinchum, B.A., and Hartsough, P.C., 2019, Porosity production in weathered rock : Where volumetric strain dominates over chemical mass loss: *Science Advances*, v. 5, p. 1–11, doi:10.1126/sciadv.aao0834.
- Riebe, C.S., Kirchner, J.W., and Finkel, R.C., 2004, Erosional and climatic effects on long-term chemical weathering rates in granitic landscapes spanning diverse climate regimes: *Earth and Planetary Science Letters*, v. 224, p. 547–562, doi:10.1016/j.epsl.2004.05.019.