Supplementary Materials for

**Porosity production in weathered rock: Where volumetric strain dominates over chemical mass loss**

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The PDF file includes:

- Supplementary Text
- Fig. S1. Rock physics model of porosity.
- Fig. S2. Representative x-ray diffraction pattern from separated clay fraction.
- Table S1. Regression statistics.
- Legend for data file S1

Other Supplementary Material for this manuscript includes the following:

(available at advances.sciencemag.org/cgi/content/full/5/9/eaao0834/DC1)

Data file S1 (Microsoft Excel format). Physical properties, bulk geochemistry, mass transfer coefficients, and volumetric strain.
SUPPLEMENTARY TEXT: MASS BALANCE DERIVATIONS

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

$$
\varepsilon = \frac{V_w - V_p}{V_p} = \frac{V_w}{V_p} - 1
$$

(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 ($\rho$) and porosity ($\phi$) for both protolith and weathered material according to Eq. S2.

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

(S2a)

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

(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 we use mineral grain density rather than bulk density.)

Following previous derivations (I3), 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.

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

(S3)

Although the derivation of Eq. S3 is conceptually simple, it 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, as shown next, 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. Our formula for estimating the total change in mass from protolith to saprolite (or soil) is a new addition to this classical framework. In subsequent sections, we show how it can be used to express porosity explicitly as a function of both volumetric strain and chemical mass loss.

Mass-transfer coefficients

The chemical mass loss of a soluble element from soil or saprolite can be expressed as its mass-transfer coefficient ($\tau_{ij}$), 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 (I3).

$$
\tau_{ij} = \frac{C_{j,w} M_w}{C_{i,p} M_p} - 1 = \frac{C_{j,w} C_{i,p}}{C_{i,p} C_{j,w}} - 1
$$

(S4)

The central terms of Eq. S4 show that the mass transfer coefficient, colloquially known as “tau”, 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 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, the mass transfer coefficient 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 principles from Eq. S4 show 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 (13). We considered all three of these prospective immobile elements in our analyses (see main manuscript file).

The bulk mass-transfer coefficient or “bulk tau”

Although tau has been highly informative over the years about mass losses in saprolite and soil (11), it only provides an element-by-element perspective that does not integrate the overall mass loss in weathered material. Thus, tau quantified using Eq. S4 may not fully capture the contribution of mass loss to total porosity, particularly when it is applied to elements that have low abundance in the protolith.

To quantify how mass loss influences porosity, we introduce the “bulk mass transfer coefficient,” or bulk tau (τₐ), which is equal to the sum over all n elements (both mobile and relatively immobile) of the mass loss of each element weighted by its concentration in the protolith.

$$\tau_b = \sum_{j=1}^{n} C_{j,p} \tau_{i,j} = C_{1,p} \tau_{i,1} + C_{2,p} \tau_{i,2} + \ldots + C_{n,p} \tau_{i,n}$$

(S5)

We use Eq. S4 to expand terms in Eq. S5 and obtain Eq. S6a, which can be simplified by regrouping terms as shown in Eq. S6b.

$$\tau_b = (C_{1,w} \frac{C_{i,p}}{C_{1,w}} - C_{1,p}) + (C_{2,w} \frac{C_{i,p}}{C_{2,w}} - C_{2,p}) + \ldots + (C_{n,w} \frac{C_{i,p}}{C_{n,w}} - C_{n,p})$$

(S6a)

$$\tau_b = \left(\frac{C_{i,p}}{C_{i,w}}\right)(C_{1,w} + C_{2,w} + \ldots + C_{n,w}) - (C_{1,p} + C_{2,p} + \ldots + C_{n,p})$$

(S6b)

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

$$\tau_b = \frac{C_{i,p}}{C_{i,w}} - 1$$

(S7)

An alternative approach to deriving Eq. S7 (which can be readily evaluated using field measurements of Zr in protolith and weathered byproducts) is to start with the overall mass of unweathered protolith $M_p$ and quantify the fractional mass loss $\Delta M/M_p$ (equal to $\tau_b$) after the protolith is converted to a weathered mass $M_w$.

$$\frac{\Delta M}{M_p} = \frac{M_w}{M_p} - 1 = \tau_b$$

(S8)

We can also write a mass balance for individual elements.
Here, we adopt conventions of previous work \((13)\) in assigning negative values to \(\Delta M_i\) and \(\Delta M\) when mass is lost from the weathering profile. For immobile elements, the mass loss \(\Delta M_i\) in Eq. S9 is zero, and therefore \(M_w/M_p = C_{i,w}/C_{i,p}\). So, the ratio of immobile element concentrations can be substituted into Eq. S8, indicating that \(\tau_b = C_{i,p}/C_{i,w} - 1\) as shown independently in the derivation of Eq. S7.

Thus, bulk tau can be readily estimated from measurements of immobile element concentrations in protolith and weathered material. Crucially, it is a metric that 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**

Eq. S1 suggests that calculating strain is straightforward, but the protolith that created the weathered material is no longer present, so it is generally impossible to measure its initial volume and solve for strain using Eq. S1 alone. Fortunately, strain, like tau, 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.

\[
V_w \rho_{b,w} C_{i,w} = V_p \rho_{b,p} C_{i,p}
\]

(S10)

Here, the subscript \(b\) in the density terms indicates a bulk, rather than a mineral-grain density. Following previous derivations \((13)\), we combine Eqs. S1 and S10 to obtain Eq. S11.

\[
\varepsilon = \frac{V_w}{V_p} - 1 = \frac{\rho_{b,p} C_{i,p}}{\rho_{b,w} C_{i,w}} - 1
\]

(S11)

Thus, strain can be estimated from measurements of bulk density and bulk geochemistry from samples of protolith and weathered soil \((13)\). 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 \((17-20)\), 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**

We can modify Eq. S3 to explicitly include bulk tau (Eq. S7) and strain (Eq. S11). This yields Eq. S12.

\[
\phi_w = 1 - \frac{\tau_b + 1}{\varepsilon + 1}
\]

(S12)

Here we assume that the porosity in the protolith is negligible. This should often be reasonable in landscapes underlain by crystalline bedrock; porosity in granitic soil and saprolite, for example, can be as high as 60\% \((39)\), whereas porosity in unweathered granite is much lower \((2)\), and thus may often be negligible in comparison. Eq. S12 also 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. S12 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. S12).
Eq. S12 shows that porosity can be quantified if the total strain and mass loss are both known. It also shows that, when porosity is known (e.g., from geophysical surveys), one can infer either strain or mass loss if the other variable is known. Next, we consider hypothetical scenarios in which porosity increases as bedrock is exhumed by erosion at the landscape surface (Fig. 1, main text).

**Scenario 1: Where mass loss alone produces porosity**

In Scenario 1, strain within saprolite and soil is negligible. This is consistent with the conventional view of saprolite as a material that is weathered in place isovolumetrically (17-20). When \( \varepsilon = 0 \), Eq. S12 reduces to Eq. S13.

\[
\phi_w = -\tau_b
\]

when \( \varepsilon = 0 \)  

(S13)

Thus, in this scenario, all changes in porosity are accounted for by changes in mass as material is exhumed from protolith to the surface. The negative sign arises because porosity must always be positive and \( \tau_b \) is defined to be negative for mass losses (which create voids and thus porosity). The predicted patterns in tau and strain are shown in Fig. 1C: All increases in porosity are accounted for by changes in mass as the protolith is exhumed to the surface.

**Scenario 2: Where volumetric strain alone produces porosity**

In Scenario 2, mass loss in fractured rock, saprolite, and soil is negligible. So \( \tau_b = 0 \) and Eq. S12 reduces to Eq. S14.

\[
\phi_w = 1 - \frac{1}{\varepsilon + 1} = \frac{\varepsilon}{\varepsilon + 1}
\]

when \( \tau_b = 0 \)  

(S14)

This relationship is shown conceptually in Fig. 1D: As minerals are exhumed to the surface, porosity increases solely due to increases in strain. Mathematically, because \( \tau_b = 0 \), \( C_{i,p} = C_{i,w} \). This means that Eq. S11 reduces to Eq. S15.

\[
\varepsilon = \frac{\rho_{b,p}}{\rho_{b,w}} - 1
\]

when \( \tau_b = 0 \)  

(S15)

In this scenario, changes in strain solely reflect changes in bulk density.

**Scenario 3: Where both mass loss and volumetric strain produce porosity**

Scenarios 1 and 2 represent endmembers of chemical mass loss and volumetric strain accounting solely for porosity production in saprolite and soil. A third hypothetical scenario is that both processes contribute to subsurface porosity production. For example, a step-change in tau might occur at the base of saprolite, while strain increases continuously from the base of fractured rock all the way to the landscape surface (Fig. 1E). This is just one of an infinite number of possible patterns in which both strain and mass loss contribute to porosity production in a weathering profile.
**Fig. S1. Rock physics model of porosity.** Image represents ranges for just one depth below the surface and a mineral assemblage of 50% feldspar, 25% quartz, and 25% clay.

**Fig. S2. Representative X-ray diffraction pattern from separated clay fraction.** The absence of a peak intensity at the 2-theta expected for expanding clays (i.e., smectite or vermiculite) indicates that they are not present in the saprolite. However, small peaks occur at the diffraction angles expected for illite suggesting a component of clay in our samples at the SSCZO.
Table S1. Regression statistics.

<table>
<thead>
<tr>
<th></th>
<th>weight % of oxide</th>
<th>r²</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fig. 3</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Bulk density vs. depth</td>
<td>0.62</td>
<td></td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Porosity vs. depth</td>
<td>0.61</td>
<td></td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Bulk tau (i = Zr) vs. depth</td>
<td>0.02</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>Volumetric strain (i = Zr) vs. depth</td>
<td>0.49</td>
<td></td>
<td>&lt;0.001</td>
</tr>
<tr>
<td><strong>Fig. 4 – Porosity, bulk tau and volumetric strain</strong></td>
<td></td>
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</tr>
<tr>
<td>Porosity vs. bulk tau</td>
<td>0.07</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>Porosity vs. volumetric strain</td>
<td>0.62</td>
<td></td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

**Fig. 5 – Mass transfer coefficients versus depth**

| j = SiO₂, i = Zr | 59.3 | 0.001 | 0.88 |
| j = Al₂O₃, i = Zr | 17.3 | 0.004 | 0.81 |
| j = Fe₂O₃, i = Zr | 7.2  | 0.02  | 0.53 |
| j = CaO, i = Zr  | 6.2  | 0.17  | <0.001 |
| j = MgO, i = Zr  | 3.3  | 0.05  | 0.29 |
| j = Na₂O, i = Zr | 3.1  | 0.16  | 0.05 |
| j = K₂O, i = Zr  | 2.2  | 0.06  | 0.23 |
| j = P₂O₅, i = Zr | 0.2  | 0.10  | 0.11 |
| j = Mn₃O₄, i = Zr | 0.13 | 0.11  | 0.11 |

**Fig. 6 – Bulk tau versus depth**

| i = Nb    | 0.01 | 0.90 |
| i = Ti    | 0.11 | 0.09 |

**Fig. 8 – Seismic velocities predicted from geochemical measurements**

<table>
<thead>
<tr>
<th></th>
<th>r²</th>
<th>p-value</th>
</tr>
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<tbody>
<tr>
<td>Bulk tau only</td>
<td>0.71</td>
<td>&lt;0.001</td>
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<tr>
<td>Strain only</td>
<td>0.67</td>
<td>&lt;0.001</td>
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<tr>
<td>Bulk tau and strain together</td>
<td>0.66</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>
Data file S1. Physical properties, bulk geochemistry, mass transfer coefficients, and volumetric strain. Excel spreadsheet (.xlsx) containing bulk geochemical data and calculated values of tau, strain, and porosity for each of the data points presented here.