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Comment on esurf-2022-9

Anonymous Referee #1

Referee comment on "Mineral surface area in deep weathering profiles reveals the interrelationship of iron oxidation and silicate weathering" by Beth A. Fisher et al., Earth Surf. Dynam. Discuss., <https://doi.org/10.5194/esurf-2022-9-RC1>, 2022

General comments

This manuscript presents detailed observations of mineral surface area and mineralogy in two deep profiles in a watershed and uses these data to understand processes involved in the development of weathering profiles. The profiles extend through soil and weathered rock to a depth of ~20 meters, and hence are a welcome contribution to understanding incipient stages of weathering and profile development. The authors show that measured specific surface area increases from the bottom to the top of the two profiles. The slope of this relationship (SSA vs. depth) shows a prominent break at a depth of 3 m. This depth coincides with the appearance of secondary minerals, but not with macro-scale morphological boundaries in the profile. Elemental depletion (τ) profiles (presented in an earlier publication) show that elemental depletion occurs to several meters below the 3 m boundary. The authors infer that oxidation weathering reactions play an important role in development of the weathered profile and provide lengthy conjectures on physical processes that also operate to this depth.

I found the surface area data interesting particularly coupled with information on mineralogy and morphology of the weathered profile, although the presentation is difficult to follow. I also found several aspects to the manuscript in need of improvement. It would help to pull together the key relevant observations into one figure-- SSA, element depletion profiles, mineral abundances (at least for key minerals), morphological boundaries. The geomorphic context was not well described; this is relevant to the observations in the site the authors refer to as an "interfluvial", where there is apparently an incised colluvial deposit on which the weathered profile is developed, as well as to the big picture of how this landscape is forming. There is insufficient characterization of the weathering processes invoked by the authors. Finally, the authors seem unaware of other work on mineral surface area in weathering. Addressing these issues probably constitutes major revisions, but once handled, the manuscript should be worthy of publication.

Geomorphic context:

The two profiles are located on a ridge and an "interfluvium". An interfluvium is a drainage divide between two adjacent rivers (Latin *fluvius* for river). In this manuscript, the region called an "interfluvium" seems to be a gullied colluvium deposit. In the caption to Figure 1, it is described as both convergent and convex. It is unclear whether or how often either gully contains channel flow, but the impression is that neither gully qualifies as a river. Why not call it what it is? Gullied colluvium. There must have been a good reason why the gullied colluvium/interfluvium was selected for the effort of coring, but that reasoning does not come out in this manuscript. It is not representative of the rest of the watershed—so the choice must have been made for some other reason.

Of interest is the timing and cause of the apparent transition from accumulation of colluvium (or perhaps steady state) to incision and how this might affect the weathered profile. The transition from accumulating to eroding should affect the weathered profile in some way. Some consideration of when this occurred seems relevant to understand the profile.

Curiously, although the schematic diagram in Figure 1 implies that colluvium is thick at the gullied colluvium site and absent at the ridge site, there is no evidence of this difference in any of the data shown. What is going on? Why is there no distinction between a weathering profile developed in colluvium and a weathering profile developed in bedrock? This needs explanation.

The geomorphic context also comes up with respect to the weathering processes considered. There is an extensive conceptual discussion of frost cracking and allusion to nearby glaciers. Where was the glacial margin? When was the Last Glacial Maximum (LGM) in this area? The inferred mean annual temperatures present and past could be used to assess the depth over which frost cracking has occurred (and is occurring). Here is another place where more consideration of the time at which the profile switched from accumulating material (pushing weathered rock/soil, kinks in the surface area profile, soil horizons, etc. down relative to the surface) to the present eroding (gullied) state is relevant.

Another missing aspect of the geomorphic context is a discussion of denudation rates and of regional landscape evolution. The long term denudation rates in an eroding upland (which this site appears to be on the whole) set the timescale for the weathered profile. The regional landscape evolution would describe the proximity to the ice sheet margin, periglacial landscape features, the dynamics of the river into which this catchment flows. In essence, a brief outline of the regional earth surface dynamics.

Weathering processes

The discussion of weathering processes needs some work. Many weathering models rely

on chemical processes in which diffusion limits reaction progress (whether chemical or mechanical—e.g. frost cracking), and so produce weathering profiles that do not have sharp boundaries. The authors seem not to understand this. Fractures are a way to overcome the limitations of diffusion in chemical processes, as water and reactants can be transported along fractures and then the diffusion process is involved only from the fracture surface. This is shown in models of spheroidal weathering (Fletcher et al., 2006) and fracture flow (Pandey & Rajaram, 2016; Anderson et al, 2019), and in datasets from cores (e.g., Holbrook et al, 2019).

Moreover, the authors assert that frost and tree rooting mechanisms should produce a weathering front at a uniform depth of 3 m across the landscape, but offer little to support this conjecture. In any case, I would expect slope aspect to produce non-uniform depths of frost and tree rooting influences.

Finally, the discussion of surface area production and weathering processes is a little convoluted. The heart of the matter is that a prominent kink in the SSA profiles occurs at about 3 m depth, which is apparently unrelated to the depth of element depletion (shown unfortunately only in an earlier paper). The authors argue that O₂ driven oxidation reactions are driving this mineral surface area production (after having spent a page asserting that frost cracking and tree root growth was responsible for the surface area production). A long argument is put forward that CO₂ increases with depth in soil (most likely true), while O₂ decreases with depth in soil (also most likely true), although they do not measure these gases. There seems to be a lack of acknowledgement of the effect of CO₂ created acidity (which produces a weak acid) compared to O₂ driven sulfide oxidation, which produces a strong acid. There is also an abundant literature on the effect of organic acids on silicate weathering rates, none of which is considered. Because the chemical weathering data is presented in an earlier paper, it isn't possible to understand quantitatively how much silicate weathering occurs at various depths, but it seems entirely likely to me that the rate is enhanced where boosted by organic acids produced at shallow depths and strong acids that are by-products of oxidation reactions. The leading edge of weathering does not need to be where the rate is fastest—indeed may not be. I made few line-by-line comments in this section because I think it needs major revision.

Other work on mineral surface area

The claim that this work was the first ever measurement of total mineral surface area in a weathered profile caught my attention. It is true that I cannot think of another work that presents an integration of measured mineral surface area in a profile. However, the total mineral surface area in a watershed was estimated long ago by Michael Velbel (Velbel, AJS, 1985) and Tomas Paces (Paces, GCA, 1983) in order to compare field (watershed) based weathering rates with lab-based rates. Clow and Drever (Chem Geol, 1996) measured mineral surface area in a "nanocatchment" in their pursuit of the lab-field weathering rate discrepancy. These authors were chasing a different question than the present manuscript, yet their work is relevant and seems worthy of mentioning. I don't know the surface area literature well, but there is much more to plumb on all the ins and outs of measuring and interpreting surface area data.

I was surprised that Lixin Jin's nanoporosity measurements in a 20-m deep borehole in shale were not cited (Jin et al., Am Mineral, 2011), as they find changes in nanoporosity (and calculated SSA) closely associated with the onset of feldspar dissolution and of dissolution of chlorite and illite. The differences in conclusions should be discussed.

Detailed comments

Figure 1

- It's unclear what is to scale and what is not on this schematic. Given that a lidar DEM is available, why not show an actual topographic cross section?
- After the laborious definitions of bedrock and weathered rock in the text, these are ill-defined on the diagram. Soil, carefully defined in the text, is not shown. Colluvium is faintly shown (hard to see), but was not defined in the text.
- Given that this is a schematic diagram, why show SSA and elemental depletion curves—presumably also schematic-- It would be much more informative to show the curves elsewhere, quantitatively, rather than schematically.
- Are the divots in the cross section where the gullies are located?
- Is the water table measured, and if so, when? Is the range of water table depth variations known? What are these?
- The caption describes the interfluvium as a "convergent area between two ridges". Interfluviums are divergent areas between two rivers.

Figure 2

- Hillshades are pretty, but not quantitative. Can you add topographic contours? Several topographic features described in the text are not visible at this scale (e.g., 2-3 m circles, tree throw mounds)
- Too much text on the figure—obscures the topography.
- What are black dots, white circle, white triangle? Use a key.
- (I would call the area around the number 6 in the label "Toeslope Pit 6" an interfluvium, by the way.)
- Show the seismic line, and where the topographic profile you can make for Figure 1 are located.
- Please identify Spring Brook, the spring at its head, and the "historic gully".

Figure 3

- This figure might be more effective if it was annotated in a way that the 3 m depth were illustrated (perhaps on the vertical scale).
- Identify the base of soil, saprolite, and weathered rock. It's unclear why water table is featured on these figures so much more prominently than the weathering boundaries. You may need separate plots for each profile.
- It would be useful to see a bulk density and grain density profile as well.
- How are SSA measurements interpolated or estimated?

Figure 5

- Why not plot with depth on the vertical axis (as in Figure 3)?
- Show soil, saprolite, weathered rock boundaries

Figure 6

- Opps! Error in the caption

Figure 7

- Please show the locations of the wells on this cross section (and show where this transect is located on Figure 2)

Line by line notes

L11 Define "mineral specific surface area". It's unclear what the surface area is being normalized to—whether it is each mineral (as mineral specific implies), or the usual surface area per unit mass of material.

L11 Suggest "increases" rather than "is generated"

L15 What is an SSA profile?

L17 soil to weathered rock is a single boundary, so change boundaries to boundary, or better yet, say "soil to weathered rock boundary".

L18 Are there multiple SSA boundaries at 3 meters? I'm confused.

L19 7 and 10 meters **depth**

L43-44 The definition of weathered rock limits weathered rock to chemically altered rock. Often, physical weathering processes precede chemical weathering processes (see work by Fletcher, Brantley & Buss; Goodfellow).

L46 isovolumetrically

L65-67 This sentence is problematic. Is the conversion of weathered rock to soil termed "soil production" only where the chemical weathering rate in the soil is proportional to this rate (as the sentence states)? What is the process called where the chemical weathering rate is not proportional to the soil production rate?

Moreover, most of the works cited here to support this contention do not measure both chemical weathering rate in the soil and soil production rate. Gilbert (1909) was only concerned with the detachment of particles from rock into soil, his "soil production", and does not present measurements of either this rate or chemical weathering rates. Heimsath et al. (1997) used cosmogenic radionuclides and an assumption of steady state (also assumed by Gilbert) to determine soil production rate; they did not determine chemical weathering rates. Raymo and Ruddiman (1992) is about uplift driven climate change; they do not quantify soil production rates or chemical weathering rates (although they do discuss proxies for the latter, such as the Sr isotope record in seawater). Riebe et al (2004) do measure both soil production rates and chemical weathering rates, but do not find that they are "directly proportional", as claimed here. West et al. (2005) looked at erosion rates and silicate weathering rates, but never mention "soil production".

L82 In this sentence, "weathering fronts" are limited to features associated with chemical processes, another instance of ignoring the role of physical processes. Frost cracking is not a chemical process.

L95-100 I often find it artificial to state a hypothesis for a field-based study, and instead

find it more useful to outline a broad inquiry. Rather than “We hypothesize that x will result in y”, it’s more genuine to state something like “ We pursued defining the relationship between porosity, mineral surface area, and weathering processes”. The attempt to write a hypothesis for this study—an effort surely done after the measurements were made—led to the inclusion of an observational detail about weathering front depths in this particular landscape in a section titled “Hypothesis”. The end result is a very local hypothesis that does not engender generality.

L105 Much of the text in here repeats verbatim the figure caption. Choose one place to describe the oddity of the incised gully site and do not cut-paste it elsewhere.

L123 Foliation is an alignment of minerals or planes of weakness and so cannot weather.

L124 platy **fragments** of rock (?)

L130 Strictly speaking, it is streams rather than watersheds that are ordered.

L131-132 Confusing description. Is the “historic gully” one of the gullies that bounds the “interfluvium”? Neither Spring Brook nor the historic gully are identified on Figure 1 or Figure 2. There appears to be a branch in the incised forms on the hillshade in Figure 2, with a confluence that lies between the points labeled Swale Pit 4 and Interfluvium Pit 5. Is the historic gully one of these branches? Perhaps, but that does not fit the description of a discontinuous gully segment located upgradient from Spring Brook.

It’s also confusing to read that the historic gully is a depositional swale. If the historic gully is in the deep colluvium shown in Figure 1, then the geomorphic history is yet more complicated: 1) accumulation of deep colluvium in a hollow or swale, followed by 2) incision of a gully or two gullies (?), followed by 3) erosion (probably diffusive processes) of a convexity between the gullies, followed by 4) development of an A horizon in the eroded colluvium that is apparently indistinguishable from the A horizon found at the ridge site. Writing this history raises several points of ambiguity. The historic gully is described as “up gradient” of Spring Brook, a spring fed perennial stream. The cross section (Figure 1) and the hillshade map (Figure 2) do not show an incised gully that is up gradient from a channel head. Is the a-horizon found all the way across the interfluvium, or is it incised (adding yet another period of stasis followed by incision).

L137 2-3 m diameter circular features are not readily visible on Figure 2.

L141 The **present** climate of Spring Brook...

L144 I don't think ybp is in standard usage; when used, bp is capitalized. Follow journal standard. I would use 18-12 ka here, and 9 ka a few lines down, since these are specific dates, rather than timespans.

L145 ...which represents a ***periglacial climate at the Last Glacial Maximum***.

L164 How is a core sieved?

L167 Were soil pits excavated to the top of weathered rock? Word missing in this sentence—"within a few meters of _____"

L177 I find it odd that fine material created by the grinding action of the drill is the source of samples used in this study. Were any core samples analyzed?

L203 See my general comments above.

L204 Perhaps use "land" surface area rather than "ground" surface area, given the description of samples being generated by grinding (L177).

L218 How were soil cores obtained?

L226 What impeded measurement of bulk density over the intervals mentioned, which cover 75% of the profiles? What is the material? Bedrock and weathered rock over some fraction of it, but I cannot tell where these boundaries are. Colluvium? Use same approach as for soil. Saprolite? What is the problem?

L229 What mass of rock chips was used for each density measurement? Water displacement is difficult to do well.

L230 Plastic or wax coating of friable material for measuring density is a much older idea than Jin et al. (2010).

L235 Why assume 32% porosity in the rock? This is an enormous value. I expect porosity to increase toward the surface, and to be much higher in soil and colluvium than

in saprolite or weathered rock. There is often an abrupt change in bulk density across the soil/weathered rock interface, but this assumption obliterates it.

L307 There is no denudation rate data in the section titled "Morphology and denudation rate"

L319 Figure 1 shows the kink in the surface area profile, which I'm using as a 3 m depth scale, as occurring within the colluvium at the supposed interfluvial site, and within the weathered rock in the ridge site, in contrast to the data reported here. Please reconcile.

L321-322 Confusing to follow trends from bottom up and from top down in the same sentence. Use a consistent direction, and perhaps break this up to be more readable.

L350 delete "plot of"

L378 Table 1 could be plotted... The abundance of plagioclase minerals from 7 m to the surface does not appear to gradually decrease. There are also low plag numbers below 7 m.

L417 It is very difficult to see a "gradual, uniform increase" in seismic velocity with depth in Figure 7. The color ramp emphasizes the boundary between blue and greenish colors (about 300 m/s). It would take considerable effort to analyze the hues plotted to see a uniform increase. I note that the color bar itself is non-linear.

A prominent, yet unnoticed feature in Figure 7 is the high velocity material that rises to the surface at the right end point of the transect. Please discuss this feature.

Commonly seismic velocity profiles are used to identify fresh/weathered rock boundaries.

L438 The phrase "Weathering models expect..." anthropomorphizes weathering models.

L438 Please identify which weathering models produce abrupt changes in rock properties. I can think of only one—Fletcher et al. (2006, EPSL), in which a specified threshold in accumulated strain is presumed to generate fractures. This feature takes a diffusive (chemical weathering) process and produces a sharp weathering front. It's beautiful, because it matches data in way that most weathering models—whether

chemical or mechanical—cannot, because diffusive processes do not produce sharp boundaries or interfaces.

L442 “nebulous”—consider your word choice.

L443 What are secondary fractures? This term suggests that secondary fractures differ from primary fractures (whatever those are), and that water behaves different in these different fractures. Please explain.

L447 Seismic velocity profiles tend to smear out boundaries.

L448 Could you summarize these published results in one of the figures?

L449-450 I do not agree that there is a generally agreed expectation for depth of the weathering front from ridge to valley. Indeed, much of the US CZO effort was to map this boundary and understand it in as many places as possible, as a step to develop our understanding of how weathering and erosion interact.

L455 The statement that frost and tree rooting will both produce uniform weathering to a depth of 3 meters in this landscape is conjecture. More support is needed—or label this as “we suggest” or some such phrase.

L465 Look at Denny & Goodlett (1956, USGS PP288, p 59) for a discussion of tree throw in this area that might be more appropriate than Roering.

L471 This paragraph does not contain any direct observations from the study site. Rephrase this sentence—something along the lines of “These observations from other areas lead us to conjecture that the 3 m depth change in specific surface area observed in Spring Brook might possibly be related to tree rooting processes.

L472 Last glacial maximum is a time, not a place.

L475 Why are LGM periglacial processes impactful only in the continental US? (legacies, not legacy)

L479 The frost cracking window is about -3 to -8°C at whatever depth those temperature conditions occur. Hallet et al. (1991, Permafrost Perigl Process) defined the frost cracking window in lab experiments.

L481 Anderson et al. (2013) are not the only authors who understand that frost cracking and frost creep are climate driven processes. Perhaps you could cite a periglacial textbook—e.g., Washburn 1973, Periglacial Processes and Environments?

L483 Again, this is conjecture on the depth of frost weathering expected in this setting. Please rephrase.

L485 I don't quite see the trends described. There are no SSA-Si data from below 3 m at the interfluvial site, hence no trend can be discerned. The data from the ridge does not have a clear trend below 3 m. Also, the wording is a little unclear given that the apparent trend is given instead as a range of values (4-10 m²/g, rather than 4 m²/g increasing to 10 m²/g from 3 m depth to the surface).

L486 "supported by"? Do you mean coincides with? In any case, I cannot see the quantitative change in illite and vermiculate abundance referred to from the XRD patterns. Please provide quantitative data.

L524-525 How does oxidation of iron-bearing primary minerals form phyllosilicates? Please write out some example reactions.

L566 I think the number 2 in this line is meant to be Equation 2?

L568 See nice review of oxygen limitations in chapter by White and Buss in the Treatise on Geochemistry (2nd Ed)