

Earth Surf. Dynam. Discuss., referee comment RC2
<https://doi.org/10.5194/esurf-2021-87-RC2>, 2022
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Comment on esurf-2021-87

J. Jotautas Baronas (Referee)

Referee comment on "The effect of lithology on the relationship between denudation rate and chemical weathering pathways – evidence from the eastern Tibetan Plateau" by Aaron Bufe et al., Earth Surf. Dynam. Discuss., <https://doi.org/10.5194/esurf-2021-87-RC2>, 2022

General comments

This manuscript by Bufe et al. presents new river chemistry data from a range of small catchments in the eastern Tibetan plateau, using it to partition silicate-carbonate-sulfide weathering and the relative effect on atmospheric CO₂. Using previously published cosmogenic denudation data, they demonstrate that carbonate-sulfide weathering correlates with denudation, whereas silicate weathering does not. The results are consistent with a growing body of evidence that, put bluntly, mountains around the world may be acting as CO₂ sources rather than sinks. This is an important and contentious question, and therefore any new constraints are welcome. In this sense, it is a topic within the scope of ESurf, with substantial new data and conclusions worthy of publication.

From technical standpoint, the manuscript is very well written and structured, with good use of English language. The title needs to be more specific, however. The previous/related work is properly accredited/cited with just a few exceptions as noted below. From a scientific standpoint, the study provides a "snapshot" of pre-monsoon weathering stoichiometry in the study area, allowing interrogation of relative spatial trends. A weakness (as would be in any river chemistry study) is the lack of runoff or seasonal timeseries data. Regardless, it is a little-studied and uninstrumented area, the data are therefore valuable, and they quite convincingly support the discussion and the conclusions (although I provide some suggestions below where I think the authors can better recognize and state these limitations). The authors partly compensate for this with a comparison of both inverse and forward modelling approaches, which is not done very frequently in such studies and is useful. In summary, it is a welcome contribution, which I recommend for publication, once the issues raised below have been addressed.

Major issue 1: sources of sulfate

Because this is, in a sense, an “old school” approach that relies solely on solute concentrations (as opposed to isotopic signatures of sulfate and/or bicarbonate), the authors need to be as convincing as possible that riverine sulfate is indeed (very likely) derived exclusively from sulfide weathering.

- On L126 authors cite previous papers to say “major evaporites are not reported”. But because evaporite phases have dissolution kinetics even faster than carbonates or sulfides, even trace amounts could end up dominating the riverine budgets. For example, how confident are the authors that there is no carbonate-associated-sulfate (CAS) in the local rocks, perhaps similarly to elsewhere in the Himalaya (<https://doi.org/10.1016/j.sedgeo.2021.106027>, recognizing the differences in the lithologies and tectonic histories)? Presumably, the extent of petrologic/mineralogic studies in Sichuan is considerably lower? All this is to say, that “no sulfate in rocks” appears like a major assumption, which needs to be backed as thoroughly as possible, given all available data. If a convincing enough argument cannot be made, then perhaps the modelling needs to incorporate an appropriate degree of uncertainty in this regard.
- This all relates to another point that the authors make quite prominently. L24: “sulfur oxidation state during prograde metamorphism of pelites in the mid crust could lead to sulfate reduction that is even more complete than in low-grade sediments and provides a larger sulfide source”; L346: “The production of sulfide by thermal reduction of trace marine sulfates embedded in marine sediments becomes efficient at temperatures above ~500 °C (Goldstein and Aizenshtat, 1994), and could be a viable explanation.” Doesn’t this imply that in the less metamorphosed flysch units there should be unreduced marine sulfate? Perhaps there is a good explanation but currently this seems like a major contradiction with the “no sulfate” assumption.

Major issue 2: discussion of concentrations & geomorphic controls on weathering

- You mention on L97 that precipitation (and therefore probably runoff) rates vary only by a factor 4-5 across the catchments and you therefore disregard them given the much higher variability in denudation. But crucially, your solute concentrations for the most part vary within a factor of 4-5 or so, and therefore could theoretically be strongly modified by differences in runoff among the catchments. Granted, you are careful to avoid any discussion of weathering “fluxes” in your study. But even if you do not explicitly say it, solute concentrations do effectively stand in for fluxes (or rather area-normalized rates) in parts of the discussion. Strictly speaking, only solute ratios (and the model results) are immune to this, whereas, for example, an assertion that absolute rates (fluxes) of pyrite and carbonate weathering increase with D, could be seen as unsupported. However, I do not think that any extrapolation to rates or fluxes (implied or explicit) is unwarranted and it is an important part of the discussion (see below). If we can’t discuss solute concentrations, then only F_{carb} and F_{sulf} are left,

which is not that much... My suggestions would be to 1) acknowledge a bit better the caveat of the lack of runoff data (and concentration-runoff timeseries, for that matter); and 2) plot the mean annual precipitation rates somewhere to better convince the reader that differences in runoff are not driving the observed differences in concentrations.

- L302-309 raises and briefly discusses the second major point of this study – that silicate weathering rates appear decoupled from denudation in the study area. I feel it deserves quite a bit more attention (keeping in mind the caveats raised in the previous point). As you note, your findings contradict some of the soil production literature which has observed both a positive and a negative (Ferrier & Kirchner, 2008) relationship between erosion and weathering. Where do your study catchments fall on these global relationships of W vs D (recognizing the large caveats in estimating W here)? What could be the mechanisms decoupling soil-scale from catchment-scale weathering rates?
- To enable this more thorough discussion (and more generally), at least a brief (even if anecdotal) description of the geomorphology of the sampled catchments would be very useful. Are there any constraints on the soil / regolith depths? Is erosion landslide-dominated? Are these catchments vegetated or above the tree line? If nothing else, there are DEM data for steepness etc, already probably discussed in Cook et al 2018.

Other points

- The title is arguably too broad for the scope of the paper and should include the study location, eg. "... in eastern Tibetan Plateau"
- In study site description, please mention which major river basins the studied headwater catchments belong to.
- Missing literature
 - Spence & Telmer 2005, GCA (<https://linkinghub.elsevier.com/retrieve/pii/S0016703705005946>) – one of the seminal "modern" papers outlining the implications of coupled carbonate-sulfide weathering to atmospheric CO₂, as well as the erosional control on it
 - Kemeny et al 2021, GCA (<https://doi.org/10.1016/j.gca.2020.11.009>) – a thorough study of sulfide-carbonate-silicate weathering across the Nepal Himalayas, with some insights and implications applicable in the context of this manuscript. For example, independently constraining F_{sulf} for silicates and carbonates, demonstrating that it is higher for carbonates (not explicitly discussed but see their Fig. 7e). They also demonstrate strong seasonal variations in overall F_{sulf} – theoretically a similar dynamic could be expected in Songpan-Ganze.
 - Relph et al 2021, EPSL (<https://doi.org/10.1016/j.epsl.2021.116957>) - demonstrating both erosional and lithological control of pyrite weathering rates in the Mekong basin (headwaters draining southeastern Tibetan plateau, not a world away from the study area in this manuscript), see Section 5.5, Fig. S12
- Eq 19 – first of all, I believe there is a typo and the subscript of the last parameter should say "sil" as opposed to "carb" (otherwise, there needs to be a full derivation of this equation and an explanation how silicate weathering does not affect atmospheric CO₂! $\delta[\text{CO}_2]$). Secondly, I think it is important to discuss an assumption behind this formulation, namely that F_{sulf} is equal for both carbonates and silicates. Is this a reasonable assumption? It seems to me there are a few factors suggesting that perhaps not: 1) carbonates and silicates are often lithologically associated, as you mention in your manuscript and as documented elsewhere (eg CAS); 2) carbonate dissolution kinetics are much faster than silicate kinetics; 3) Kemeny et al. 2021

demonstrating F_{sulf} being higher for carb compared to sil using an inversion with more degrees of freedom. Therefore, perhaps valuable to explore what happens if this assumption is relaxed, allowing sulfide-carbonate to first consume one of the reactants, only then switching to either sulfide-silicate or carbonic-carbonate weathering (depending on the excess reactant). This would provide an upper limit on potential CO₂ release.

Technical

- L41 – for posterity, should add “over timescales longer than marine carbonate compensation” or similar.
- L136: typo, X = Mg²⁺ repeated twice, should probably be Cl-
- L135-150 needs to be worded more clearly. The Monte Carlo component comes out a bit of nowhere. Do I understand correctly that you do the minimization 100,000 times for each set of samples (catchments) with a given silicate lithology? Or separately for each river sample? Should L147 say “[X/Ca]_{riv}”? Do you mean that the squared distances are normalized by variance for each ratio, so that all ratios are weighted equally? What is a “mean input value”? The mean, or “best” a priori estimate of each end-member ratio? Maybe it’s best to show the chi-square formula, given there are two sets of parameters used to calculate it, and it seems this is where the hydrothermal springs are disregarded (as mentioned on L192), if I understand correctly. Also it is unclear how analytical [X/Ca]_{riv} uncertainties are included here. Are some of the modelled values outside of the analytical uncertainty range (which is what by the way)? Are the [X/Ca]_{riv} and [X/Ca]_{endmember} residuals given equal weight in the chi-squared? If so, what’s the logic behind it, and why not give the actual measured [X/Ca]_{riv} bigger weight? How many runs pass your criteria in the end, and are used to estimate the overall uncertainty? Are the “best values” selected from a single run with the lowest chi-square, or some average? Please assume that the reader would like to reproduce your procedure exactly, without having to read the previous papers, and write accordingly all the steps (in supplementary/appendix if necessary). I know this technique has been around for decades, but honestly, the actual implementation details are almost always skipped and they always differ slightly. Reproducibility is important.
- L172: shouldn’t the carbonate stoichiometry be “Ca_{0.96} Mg_{0.04}”, given the preceding sentence? I find it confusing to use a 1:1 calcite/dolomite ratio here and elsewhere.
- L172: do “square brackets” refer to “□ □” -- if so, this is not correct, as square brackets are “[]” already used for the dissolved concentrations.
- Eq 6-7: where do the “riv” values come from? Do they indicate riverine sediment, or somehow dissolved concentrations (in which case this would be very confusing and apparently circular logic)? If sediment, then I strongly suggest using a different subscript.
- Eq 8-11: what does the subscript “spl” refer to?
- L306: should say “dilution” rather than “dissolution”?
- L323: “ref 62” – wrong citation format

- Fig 3a: point sizes seem all the same in the actual plot
- Fig 3b: the title says this is a regression through the bedrock data (which sounds like a fit to all the individual bedrock samples), whereas the caption says these are carbonate-silicate mixing lines. Which one is it?
- Fig 3c: gray circle must be the carbonate endmember but this is not noted anywhere. It should also be easier to see (more distinct color/symbol)
- Fig A2: should say "lower silicate weathering" at the bottom?