

Reviewer #1

This manuscript explores how the relationship between riverine solute geochemistry and denudation rate varies between catchments with different bedrock compositions. The authors find that the concentrations of silicate-derived cations are relatively constant with increasing denudation whereas contributions from carbonate weathering and sulfide oxidation increase with increasing denudation rate. The authors also find differences in sulfate concentrations between lithologies at a given denudation rate, which affects the calculated amount of CO₂ drawdown.

The results of this study are fairly non-controversial. Nevertheless, it is nice to actually observe in data some patterns that may have been predicted/expected. Moreover, many similar datasets lack the tight constraints on denudation from ¹⁰Be measurements that are available for this study. While one could nitpick about some of the assumptions that go into the mixing model (i.e., no secondary mineral formation and the congruent dissolution of bulk silicate rock), I think the conclusions that the authors come to are the most parsimonious and that their approach is sufficient to explain the major trends in the data. Accordingly, I think the manuscript is appropriate for publication after some minor revisions. In particular, there were some methodological details that I was confused about that could be explained better in a revised version of this manuscript.

We want to thank R1 for taking the time to carefully read through and comment on the manuscript

Line 42: It is probably better to be more precise here and state that carbonate weathering by carbonic acid is CO₂ neutral over timescales longer than the characteristic timescale of carbonate precipitation in the ocean.

Added

Line 43: I would recommend against the Lasaga 1984 reference here. There are many other options out there that report measurements of silicate mineral dissolution rates. I would also suggest Johnson et al. (2019) as a more recent reference on pyrite oxidation kinetics. Lastly, it might also be worth citing the work by Kanzaki et al. (2020) on the reactive-transport modeling of silicate weathering and pyrite oxidation.

Johnson, Aleisha C., et al. "Experimental determination of pyrite and molybdenite oxidation kinetics at nanomolar oxygen concentrations." *Geochimica et Cosmochimica Acta* 249 (2019): 160-172

Kanzaki, Yoshiki, Susan L. Brantley, and Lee R. Kump. "A numerical examination of the effect of sulfide dissolution on silicate weathering." *Earth and Planetary Science Letters* 539 (2020): 116239

We changed the Lasaga [1984] reference to Berner [1978].

Johnson et al. [2019] investigates pyrite oxidation conditions of the Archean – so we believe that Williamson and Rimstidt [1994] is more applicable to the modern setting that we discuss here.

The work of Kanzaki et al. [2020] is very interesting, but it goes into details of the coupling between silicate and sulfide weathering that is beyond the scope of this conceptual introduction.

Line 50: It might make sense to cite Ibarra et al. 2016 here as well as it also compares basaltic and granitic weathering fluxes.

Ibarra, Daniel E., et al. "Differential weathering of basaltic and granitic catchments from concentration–discharge relationships." *Geochimica et Cosmochimica Acta* 190 (2016): 265-293.

Added

Line 144: My interpretation is that, depending upon the geologic map data, one of three different potential silicate end-members was used for each river sample as opposed to, for example, trying all three different silicate end-members for each catchment. I would appreciate a very clear statement about which data constraints were applied to which catchments just to avoid any confusion.

We revised the description of the inversion which hopefully clarifies the point.

Line 184: "We corrected all major elements for atmospheric inputs...". I am confused by this. I thought that rainwater was an end-member in the set of mixing equations described at the start of section 3.2. This sentence here makes it sound like the data were corrected for rainwater contributions and then inverted for carbonate vs. silicate contributions. It would be helpful if the authors could clarify their exact approach.

Thanks for the comment. Indeed, the phrasing was not very clear. We changed it to say "For the cyclic endmember, we used a volume weighted average of rainwater compositions from the eastern flank of Gongga Shan"

Line 192: "...we did not consider the hot spring end-member in finding the best-fit model in the inversion". This confused me. The start of section 3.2 describes a four end-member mixing model (silicate, carbonate, rain, and hydrothermal inputs). However, this sentence makes it seem like hydrothermal inputs were completely ignored such that the authors actually use a three end-member mixing model. If that is the case, I think it is very confusing to describe a hydrothermal end-member only to ultimately ignore it. Again, it would be helpful if the authors could clarify exactly how potential hydrothermal contributions were considered.

This sentence was very unclear. Following your comments and those from R2 we revised the description of the inversion which hopefully clarifies this point.

Line 284: I am not sure if the authors *have* to make this argument that concentrations are proportional to fluxes. I think it is best to stick to what is actually measured (i.e., concentrations and concentration ratios) as opposed to making untested assumptions about

discharge variations based on imperfect proxies (mean annual rainfall) that do vary quite considerably (factor of 3) given the range of concentration variability.

A similar point was made by R2 and the lack of runoff data remains one of the primary limits of this study. Assuming that the range of precipitation values reflects – at least to first order – the expected range of runoff, we can estimate the likely importance of differences in runoff between catchments. Approximating weathering fluxes by using the mean annual precipitation does not change the observed pattern of the data with respect to denudation rates substantially (see new Figure A5). It therefore seems likely that runoff differences play a minor role in modulating the observed variability of water chemistry with denudation in the study area. We now write: “Further, there is no co-variation between precipitation and denudation rate (Fig. 2B, Table S1). Finally, the first-order patterns described above do not change substantially when we consider ‘approximate weathering fluxes’ that are obtained by using mean annual precipitation values as a proxy for runoff (Fig. A5). Therefore, it is unlikely that differences in runoff between catchments strongly affect our data, and we interpret the observed patterns as reflecting the response of the weathering system to changes in denudation fluxes.”

Line 307: “... to the dissolution of soil waters by fluids from other parts of the landscape...”. This sentence was confusing to me. I am not sure how fluids dissolve soil waters. I recommend that it be edited for clarity.

Sorry for the confusion. This is a typo and meant to say “dilution”.

Line 316: It might make sense to cite Kemeny et al. 2021 here as well given that they also looked at seasonal changes in the carbonate weathering fraction at a similar site.

Kemeny, Preston Cosslett, et al. “Sulfate sulfur isotopes and major ion chemistry reveal that pyrite oxidation counteracts CO₂ drawdown from silicate weathering in the Langtang-Trisuli-Narayani River system, Nepal Himalaya.” *Geochimica et Cosmochimica Acta*/294 (2021): 43-69

Added

References

- Berner, R. A. (1978), Rate control of mineral dissolution under Earth surface conditions, *Am. J. Sci.*, 278(9), 1235-1252, doi:10.2475/ajs.278.9.1235.
- Johnson, A. C., S. J. Romaniello, C. T. Reinhard, D. D. Gregory, E. Garcia-Robledo, N. P. Revsbech, D. E. Canfield, T. W. Lyons, and A. D. Anbar (2019), Experimental determination of pyrite and molybdenite oxidation kinetics at nanomolar oxygen concentrations, *Geochim. Cosmochim. Ac.*, 249, 160-172, doi:<https://doi.org/10.1016/j.gca.2019.01.022>.
- Kanzaki, Y., S. L. Brantley, and L. R. Kump (2020), A numerical examination of the effect of sulfide dissolution on silicate weathering, *Earth Planet. Sc. Lett.*, 539, 116239, doi:<https://doi.org/10.1016/j.epsl.2020.116239>.
- Lasaga, A. C. (1984), Chemical kinetics of water-rock interactions, *J. Geophys. Res.*, 89(B6), 4009-4025, doi:10.1029/JB089iB06p04009.
- Williamson, M. A., and J. D. Rimstidt (1994), The kinetics and electrochemical rate-determining step of aqueous pyrite oxidation, *Geochim. Cosmochim. Ac.*, 58(24), 5443-5454, doi:[http://dx.doi.org/10.1016/0016-7037\(94\)90241-0](http://dx.doi.org/10.1016/0016-7037(94)90241-0).