

Interactive comment on “Oxidation of sulphides and rapid weathering in recent landslides” by R. Emberson et al.

Anonymous Referee #1

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In their manuscript entitled “Oxidation of sulfides and rapid weathering in recent landslides”, Emberson et al report data on the solute geochemistry and size of landslide deposits in the mountains of Taiwan. Exploiting the fact that a majority of the exposed landslides were triggered during a single storm event, the authors test the links between landsliding and chemical weathering independent of time. While the authors do not find a relationship between the size of landslide deposits and the solute concentrations they generate, they do find that rivers in catchments with more landslides tend to have the higher solute concentrations.

Overall, I think that this manuscript is timely and appropriate for publication in ESurf. However, there are a variety of criticisms that I would like to see addressed. In general, I found many instances where either key assumptions were not made clear or statements were not appropriately backed up by published literature. I’ve tried to highlight

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these instances in my more detailed comments below.

Line 34 This is hardly an exhaustive list of weathering-erosion models. Additionally, the Dixon and Von Blanckenburg paper does not present a new model of the coupling between weathering and erosion. I'd recommend that the authors cite some of the key papers in this field (included below). Additionally, the authors state that existing weathering-erosion models do not account for the effects of landsliding. While this broadly true, the issue was previously addressed by Gabet (2007; EPSL), who argued that landsliding did not affect the coupling between weathering and erosion predicted by existing models. Since it seems as if the authors are trying to argue the opposite point, it'd be worth discussing the conclusions of Gabet (2007).

Gabet, E. J. (2007). A theoretical model coupling chemical weathering and physical erosion in landslide-dominated landscapes. *Earth and Planetary Science Letters*, 264(1-2), 259–265.

Ferrier, K. L., & Kirchner, J. W. (2008). Effects of physical erosion on chemical denudation rates: A numerical modeling study of soil-mantled hillslopes. *Earth and Planetary Science Letters*, 272(3-4), 591–599. <http://doi.org/10.1016/j.epsl.2008.05.024>

Lebedeva, M. I., Fletcher, R. C., & Brantley, S. L. (2010). A mathematical model for steady-state regolith production at constant erosion rate. *Earth Surface Processes and Landforms*, 35(5), 508–524. <http://doi.org/10.1002/esp.1954>

West, A. J. (2012). Thickness of the chemical weathering zone and implications for erosional and climatic drivers of weathering and for carbon-cycle feedbacks. *Geology*, 40(9), 811–814. <http://doi.org/10.1130/G33041.1>

Li, D. D., Jacobson, A. D., & McInerney, D. J. (2014). A reactive-transport model for examining tectonic and climatic controls on chemical weathering and atmospheric CO₂ consumption in granitic regolith. *Chemical Geology*, 365, 30–42. <http://doi.org/10.1016/j.chemgeo.2013.11.028>

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Line 45 You provide no citations for mineralogical abundances at the different sites. Is this something you measured yourself? If not, you should provide the appropriate citations.

Line 80 You make the distinction between landslides receiving water directly from rainfall or from runoff into the crest of the landslide. However, in all figures and tables, it is not made clear which type of landslide each sample corresponds to. I think this distinction would be very helpful since it is reasonable to expect runoff to have higher initial solute concentrations than rainfall.

Line 98 What is thick? Is there anyway to put an approximate scale on soil depths in this system?

Line 105 These statements seem to imply that all deep groundwater is geothermal in origin, which I do not think is true (e.g., I don't think the groundwaters in Calmels et al 2011 EPSL are geothermal). Additionally, the authors state that samples are corrected for geothermal inputs but never describe how this is done.

Line 108 It'd be interesting to know what percentage of all landslides in the catchment were visited during your fieldwork. This would help readers assess whether or not the observation that half of the visited landslides were dry is likely to be representative of the entire system.

Line 141 The authors attempt a correction for atmospheric deposition using chloride concentrations and element/chloride ratios. While this is reasonable, it should be mentioned that geothermal waters, which the authors acknowledge are likely solute sources, are extremely enriched in chloride such that a small geothermal input would have a disproportionate effect on chloride concentrations and preclude the use of their proposed chloride mixing equation to correct for atmospheric deposition.

Furthermore, while the element/chloride ratios of rainfall are often assumed to be close to those of seawater, it is widely observed that ratios such as SO_4/Cl are enriched in

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rainfall relative to seawater by a factor of ~ 2 (Andreae et al. 1990 JGR). This is true even for rain that falls directly over the ocean (e.g., Stallard and Edmond 1981 JGR) and likely arises from marine biogenic aerosols. So, while the authors try and defend their choice of using seawater ratios, I am skeptical that it is a good assumption for all of the major elements.

Considering the overall point of the manuscript, I do not think it is that important that the authors correct their data for atmospheric inputs. By selecting a single rainfall end-member, the authors already assume that the chemistry of rainfall does not vary spatially across their catchment. So instead of assuming that 1) all chloride comes from rain and 2) that rainwaters = diluted seawater, which are both probably wrong, they can just compare their data with the assumption that the contribution from atmospheric deposition is not the key source of variability. Alternatively, the authors could utilize a more rigorous >2 end-member mixing approach (too simultaneously account for geothermal inputs), but that seems beyond the scope of this manuscript.

Line 173 The authors are missing a citation here. Li et al. (2014; G3) also addressed the issues associated with the automatic mapping of landslides.

Line 191 While it is true that the oxidation state of Si is +4 in natural waters, I don't think this qualifies it as a cation. For example, most dissolved sulfur also has a positive oxidation state (+6), but the authors correctly label it as an anion because it is speciated as sulfate in most natural waters. Typically, Si is speciated as silicic acid in natural waters and, because the pKa of silicic acid is high, it is fully protonated at the pH values observed in most rivers. So, maybe it is best to call Si a neutral species.

Line 200 The authors state that solute concentrations in their Taiwanese streams are high relative to global rivers, but provide neither an average value nor a citation for the typical concentrations of solutes in global rivers. Maybe the using values from the compilation of Gaillardet et al. (1999 Chem. Geo.) would be useful here.

Line 217 (and elsewhere) What is "weathering efficiency"? My interpretation would

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be that weathering efficiency is the same as what other authors call “weathering intensity”, which is the mass of rock solubilized by weathering divided by the mass of rock exposed by uplift. If this is what the authors mean by weathering efficiency, then I do not understand how differences in solute concentrations between streams and landslide seepage provide a useful constraint on it. Streams presumably average over different timescales and have different mass fluxes compared to landslide seepage, which could both obscure inferences about the proportion of rock solubilized.

If the authors mean something else, they should perhaps define this term in the text.

Line 224 The authors argue that the effects of landslide area not evident in their data by reporting R2 values. First, what model are the authors using to describe this relationship? Using an incorrect model could lead to a poor R2 despite there being an underlying relationship. Overall, this would be much easier to assess if the authors showed us a scatter plot of landslide area and TDS. After making one myself, it's pretty clear that there is not an obvious correlation.

Additionally, I am a bit confused how the authors get negative R2 values. Unless the authors are calculating some sort of adjusted R2 and just not telling us, they shouldn't be able to get negative values.

Line 226

The authors report a correlation between sulfate and TDS and argue that this is evidence for the effects of sulfide mineral oxidation. Such a correlation could arise for any number of reasons and is observed globally (e.g., the data of Gaillardet et al. 1999 Chem. Geo. show this relationship).

In general, solute concentrations are all negatively correlated with discharge, so variations in discharge alone could produce a correlation between sulfate and TDS. Similarly, solute concentrations should scale with water/rock interaction time, which could also give you a correlation between TDS and sulfate. Dilution by rainfall, evaporative

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concentration, and end-member mixing could all also give you a relationship between sulfate and TDS. And finally, as the authors acknowledge, the dissolution of evaporites could also be responsible for this correlation.

To me, the fact that the catchment is underlain by marine shales is a strong argument for sulfate being sourced from sulfide mineral oxidation. Personally, I do not see the additional insight gained from reporting a correlation between TDS and sulfate concentrations, which is expected (and observed) in most river systems independent of sulfide mineral oxidation.

Personally, I would find a scatter plot comparing elemental ratios much more convincing if the authors are trying to make the point that sulfide mineral oxidation coupled to carbonate dissolution is the dominant chemical reaction occurring within the landslide deposits. For example, $\text{SO}_4 / (\text{Na}+\text{K}+\text{Ca}+\text{Mg})$ versus $\text{Ca} / (\text{Na}+\text{K}+\text{Ca}+\text{Mg})$ would show what proportion of the cationic and anionic budgets are sourced from the weathering products of coupled sulfide mineral oxidation and carbonate dissolution.

Line 235 The authors attribute the fact that solute concentrations are independent of landslide area to a heterogenous distribution of pyrite. Since landslide areas and volumes vary by 3 to 4 orders of magnitude respectively, does this imply that bedrock pyrite concentrations also vary by 3 to 4 orders of magnitude?

Alternatively, could it be that bedrock pyrite concentrations are more or less the same, but water fluxes co-varies with landslide area so that water/rock ratios are approximately constant? Or, what if sulfide mineral oxidation is limited by the diffusion of oxygen into the landslides? In this scenario, the lack of correlation between landslide area and sulfate concentration arises from the fact that pyrite in deep landslide deposits is essentially inaccessible to weathering. I suppose that this is what the authors mean by “the degree of its exposure for oxidation”, but it might be useful to develop this idea further.

Line 241 The say that landslides “remove the supply limit” on weathering. Con-

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ceptually, this does not make sense to me. To me, supply-limited weathering refers to conditions where all weatherable-material exposed by uplift is dissolved before being exported by erosion. This contrasts with kinetically-limited weathering, where un-weathered material is exported by erosion due to material residence times being shorter than the time required for complete reaction. Ferrier et al. (2016 G3) have a good discussion about these definitions.

Based on these definitions, landslide weathering can be either supply-limited or kinetically-limited depending on how quickly landslide deposits are transported to the river channel and exported from the catchment. Since the authors do not constrain the residence time of landslides deposits with their study catchment, I am not sure how they are able to discuss supply- versus kinetically-limited weathering in landslide deposits.

Line 246 Silicon, and to a lesser extent Ca, are not conservative in natural waters (e.g., Garrels and Mackenzie 1967, Jacobson et al. 2002 GCA, and many more), so I do not necessarily see how Si/Ca can be used as a reliable proxy for the proportion of cations sourced from silicate weathering. Furthermore, all of the reported data have elevated Na to Si ratios relative to common silicate minerals (e.g., albite), which is consistent with Si loss due to secondary silicate mineral precipitation (i.e. non-conservative Si behavior).

Line 255 While I think I agree with the authors, I find the wording in this section unclear. If I understand correctly, the authors are trying to argue that sulfate is sourced predominantly from in-situ sulfide mineral oxidation as opposed to geothermal inputs. If one assumes that their single sample of geothermal water is representative of all geothermal inputs, then seepage Li concentrations can be used to place an upper bound on potential sulfate contributions from geothermal waters. Assuming all Li is sourced from geothermal waters, the observed Li enrichments in some of the seepage samples would be insufficient to account for a bulk of the sulfate budget due to the low SO₄/Li ratio measured in the single geothermal sample. So, to me, Li concentrations

not “preclude” geothermal inputs, but instead constrain their contributions to the sulfate budget.

Line 258 I suppose this comment is similar to the one above. If one assumes that potential groundwater inputs would be characterized by high concentrations of both sodium and sulfate, then the limited co-variation between sodium and sulfate concentrations would suggest that variations in sulfate concentrations are not due to mixing with groundwater.

While this seems like a reasonable argument, it'd be better supported with some scatterplots showing actual mixing relationships based on elemental ratios (not concentrations). The authors could even use literature data to better constrain some of the end-members.

Line 270 Does it matter that you are comparing solute concentrations from catchments with different surface areas?

Line 276 If sulfide oxidation is limited by O₂ diffusion, the weathering of silicates could be de-coupled from the oxidation of sulfides. In this case, a correlation between Na and sulfate would not be expected. And, as stated above, variations in Si concentrations are strongly influenced by secondary mineral precipitation which affects neither Na nor sulfate.

Line 305 The authors state that the maximum solute concentrations observed in the landslides are 15 to 20 mM. While I don't disagree with this, I am not sure how this observation alone provides insight into the “saturation” concentration of landslide weathering. While there probably is a maximum possible concentration, it need not be the highest concentration observed in this dataset. Also, saturation might be a poor word choice in this context since it has thermodynamic implications.

Line 319 The authors state that the amount of landsliding in each catchment is not correlated with the catchment slope. Where does this observation from from?

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Line 331 Lee et al. (2015 Env. Sci. Poll. R.) also report concentration-discharge relationships for Taiwanese rivers.

Line 336 Tipper et al (2006 GCA) report solute concentration-discharge relationship for Himalayan rivers and Torres et al. (2015 GCA) specifically link mountain catchments with “chemostasis” in the Andes/Amazon.

Line 345 Again, I am not sure how a correlation between TDS and sulfate can be used to argue that solutes in stream water are sourced predominantly from landslides. This correlation is not unique to landslides and could arise from many different processes.

Line 335 The statement “supersaturated everywhere with respect to Ca” doesn’t make sense. Waters cannot be supersaturated with respect to an element. They can, however, be supersaturated with respect to a mineral phase.

Line 359 The authors define the term “non-equilibrium weathering” to describe landslide weathering because “the depletion rates of the various minerals involved are likely to be very different.”

I have a few issues with this statement. First, the fact that weathering occurs in the first place is because primary minerals are out of equilibrium with respect to surface conditions. So, by definition, all weathering is non-equilibrium. Second, chemical weathering in any setting will involve minerals that react at different rates.

That said, I agree that landslide weathering is somehow “different”. To me, the important difference is that landslides rapidly transport weatherable material from depth to the surface. In contrast, “hillslope” weathering involves the much slower transport of material from depth. Rapid transport of material from depth allows minerals that typically have deep weathering fronts (e.g., pyrite) to be exposed to weathering at the surface.

Line 393 There definitely needs to be some citations for the links between weath-

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ering and atmospheric pCO₂. Many of the papers cited elsewhere in the text should also be cited here. However, the authors could also consider citing:

Lerman, A., Wu, L., & Mackenzie, F. T. (2007). CO₂ and H₂SO₄ consumption in weathering and material transport to the ocean, and their role in the global carbon balance. *Marine Chemistry*, 106(1-2), 326–350. <http://doi.org/10.1016/j.marchem.2006.04.004>

Torres, M. A., West, A. J., Clark, K. E., Paris, G., Bouchez, J., Ponton C., Fakirs S.J., Galy, V., Adkins, J. F. (2016). The acid and alkalinity budgets of weathering in the Andes-Amazon system: Insights into the erosional control of global biogeochemical cycles, *Earth Planet. Sci. Lett.* <http://doi.org/10.1016/j.epsl.2016.06.012>

Line 400 The authors mention a “feedback between drawdown of CO₂ and erosion.” Since erosion rates are not necessarily modulated by atmospheric pCO₂, I do not think this can be accurately called a feedback. Additionally, the authors should probably cite some of Maureen Raymo’s work on this topic.

Line 404 Should probably include the relevant citations for the links between sulfide mineral oxidation and erosion rates.

Line 417 The authors state that the area affected by Typhoon Morakot is now a CO₂ source but provide no evidence for this. The affect of weathering on atmospheric pCO₂ depends on the precise balance between acid producing and acid consuming reactions (e.g., Torres et al. 2016 EPSL), which was not appropriately addressed in this manuscript.

Line 448 It might be worth citing some of the other work on carbonate versus silicate weathering in New Zealand. For example,

Jacobson, A. D., Blum, J. D., Chamberlain, C. P., Craw, D., & Koons, P. O. (2003). Climatic and tectonic controls on chemical weathering in the New Zealand Southern Alps. *Geochimica et Cosmochimica Acta*, 67(1), 29–46.

Moore, J., Jacobson, A. D., Holmden, C., & Craw, D. (2013). Tracking the relation-

ship between mountain uplift, Silicate weathering, And long-term CO₂ consumption with Ca isotopes: Southern Alps, New Zealand. *Chemical Geology*, 341, 110–127. <http://doi.org/10.1016/j.chemgeo.2013.01.005>

Line 455 Again, stochastic landsliding effects were previously incorporated into a weathering-erosion model by Gabet (2007 EPSL). This work should be mentioned and discussed here.

Line 464 Again, the link between erosion and weathering the authors describe is not necessarily a feedback. The rates of tectonic uplift do not necessarily depend upon pCO₂, so changes in weathering would not necessarily feedback on erosion rates.

While I am aware that there are some possible weathering-erosion feedbacks (e.g., through rock strength and/or glaciation), I do not think that the authors are referring to these in this manuscript.

Table 1. Was DIC measured directly? If so, how? If this column is actually charge balance, then it should be labeled as such. Charge balance does not necessarily equal DIC because of species like carbonic acid and organic bases.

Also, it seems curious that sample TWS15-91 has no anions other than Cl and SO₄ yet has a pH of 8.19. I tried to re-produce this pH with the reported solute concentrations using PHREEQC and couldn't get it to work. That said, I did not try very hard. Anyways, it might be worth looking into that sample a bit more to make sure there are not any analytical issues.

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