

Interactive comment on “Short Communication: Aging of basalt volcanic systems and decreasing CO₂ consumption by weathering” by Janine Börker et al.

Janine Börker et al.

janine.boerker@uni-hamburg.de

Received and published: 16 September 2018

Response to Reviewers We thank the reviewers for their comments, which helped to improve the manuscript. We answer each comment and how we changed the MS accordingly. Please note, that the values of the new global calculations changed slightly because we ran the re-calculations with a 20km grid resolution and modified the global map from shape to grid format to allow for faster calculations.

Response to Referee 1: 1) it is somehow surprising that the weathering of old basaltic surfaces does not depend on the local runoff value. The “expected” weathering law only depends on temperature, based on the plot displayed on fig 1b. Would it be useful

C1

to plot the CO₂ consumption by the weathering of old basaltic outcrop as a function of runoff ?

These patterns were already analyzed in Li et al. (2016). The temperature normalization is used here, because of the robustness of the pattern.

The correlation between runoff and alkalinity flux rates is weaker than using temperature. This still holds if including the uncertainties of the data (with Monte Carlo type analysis, $R^2=0.96$, $p<10^{-3}$, using a linear regression for observed alkalinity flux rates and calculated alkalinity flux rates using the new temperature scaling law). Considering the Monte Carlo type application, the correlation between runoff and alkalinity flux rates becomes even weaker, if compared to a regression analysis using only the single data points.

It is not concluded that runoff plays not a significant role for determining basalt weathering rates. However, the correlation between runoff and alkalinity flux rates is not significant any longer when Inactive Volcanic fields (IVFs) and Active Volcanic Fields (AVFs) are considered separately (new Figure 2c) (Li et al., 2016).

We included a figure showing the runoff/alkalinity relationship of old volcanic fields, now in the main text (Fig.2c).

2) The authors implicitly assume that the young volcanic area are basaltic. This is not always the case (see for instance Rad et al., 2013, J South Am Earth Sci) . There is a possibility of bias in the present database: the old surfaces being basaltic, while the young volcanic areas can be dominated or affected by an andesitic lithology.

We consider now only mapped areas in catchments that were clearly described as “basaltic”. We included this part in the discussion in line 161-166: “The lithologies, predominantly described as basaltic in the global map, might introduce an additional bias to the global calculations because heterogeneities in the lithology cannot be excluded. Two active volcanic fields (Sao Miguel and Tianchi Lake) were excluded from the cal-

C2

culations because they include lithologies of trachytic composition. Nevertheless, their data points (Fig. 1c) seem to show the same weathering behavior.”

3) There is no discussion about the contribution of ash weathering to the alkalinity flux. Ashes released by active volcanoes may represent an important contributor to the CO₂ consumption by weathering given their high reactive surfaces and their content in glass (see for instance Sowards et al., 2018, *Geosphere*). I think this should discuss.

We agree with this and included it in line 131-134 in the discussion:

“Volcanic ashes and ejecta might contribute to elevated weathering fluxes because of a relatively high content of glass. Glass dissolution rates are relatively high compared to mineral dissolution rates in general, but base cation content release varies dependent on the Si:O ratio (Wolff-Boenisch et al., 2006).”

We agree that volcanic ashes provide fresh weatherable material on top of the basaltic rocks.

Response to Referee 2 (R. Emberson):

1. I think it is imperative that the authors provide uncertainty / error estimates on all of their results, and describe how these estimates were made (probably in the supplemental material). Without estimates of uncertainty, the reader is unable to assess the significance of the results. Even if the uncertainty on the measurements has already been made in the prior work (Li et al. 2016), I feel it's essential that the authors also show these estimates (and additionally explain again how these estimates were derived – see comment number 5 for further discussion). Specifically, I'd like to see uncertainty estimates attached to all plotted points in the figures, in equations 2 and 4, and in the estimates in Table 1.

We agree with this and included the uncertainty estimates by Li et al. (2016) in all figures where it was possible. It is not possible to give a suitable error for the mapping accuracy of the Holocene fraction due to the nature of the data. We calculated the

C3

error of the newly derived function using a Monte Carlo method and show the standard deviation and the root mean square error in eq.2 and 4 and the estimates of uncertainties of the global calculations in table S28 and S29. The error calculation is described in the supplemental material.

2. The different behavior of IVF and AVF areas based on reactivity is a novel way to explore the basaltic weathering regime, but perhaps it would be useful for some readers if the authors also explained this in the context of supply-limited or kinetic-limited weathering (e.g. Ferrier et al. 2016 *Geochemistry Geophysics Geosystems*). The IVF behavior shown in Fig 1b certainly looks like classic kinetic-limited weathering, but as the authors point out in the AVF this relationship no longer holds. I would suggest plotting the AVF data in the same way as the IVF data in Fig 1b. to see if there is a similar kinetically-limited relationship; if so, this could indicate that the boundary conditions for the kinetically limited system differ (e.g. due to less clay precipitation in younger lava bodies), whereas if such a kinetically-limited behavior is not evident (or the residuals are very large) then perhaps other effects (e.g. magmatic CO₂ degassing) may be relevant. Showing the reader these data could help demonstrate the effects seen, as well as making the relationships easier to understand for geochemists who work in the kinetic/supply limited paradigm.

The new Fig.2d shows the IVFs and AVFs combined in a temperature/alkalinity plot. The scattering in the plot shows that there is no classic kinetic-limited weathering visible for AVF, while, as described, the IVF follow an apparent temperature dependency. Taking into account that the four AVFs Mt. Etna, Mt. Cameroon, Virunga and La Reunion have the highest Holocene fractions (96.6%-27.7%) and all the other AVFs have less than 15% Holocene coverage, supports the argument that elevated geothermal fluxes and magmatic CO₂ contribute to enhanced alkalinity fluxes of these volcanic fields, as supported by referenced studies.

Therefore, the classical concept of supply versus kinetic limitation in tectonic context and referring to a shallow critical zone as discussed in Ferrier et al. (2016) does not

C4

work here. We included already some discussion for this before pointing out the relevance of intra-volcanic weathering (not the shallow critical zone), and the supply of fresh material due to volcanic activity.

3. The authors explain that they use the Holocene transition as a way to split the AVFs from the IVFs. This makes sense in terms of data availability, and I think it is an appropriate (if arbitrary) way to separate the data. However, the Holocene transition involved a series of global climatic changes, and I think it would be useful for the authors to explore whether this transition and the climatic changes associated with it could explain the differences observed in 'reactivity' between pre and post Holocene basaltic fields. I appreciate that the AVF and IVF areas both experience the same climate today, but I think it would be at least useful to discuss whether or not there could be a legacy effect in the IVF areas from weathering under a different climatic regime.

Our study is based on today's climate conditions and it is unknown how different climate regimes in the past may have influenced the basalt weathering fluxes due to the lack of data on the distribution of young surface areas in the past. This point is difficult to address since we have only observation data of today and it is not possible for now to reconstruct active volcanic areas for the past in a global compilation. After times of globally warmer climate and higher erosion rates, the difference in reactivity between IVFs and AVFs might be reduced, but we lack information for this in our global compilation of data. Furthermore, we calculated global fluxes for the Mid-Holocene using Earth System model outputs, comparing the different alkalinity flux models. The calculations show that models, which consider only runoff as parameter provide elevated fluxes in the Mid-Holocene, of 8 %, due to slightly higher global runoff values (Bluth and Kump, 1994; Amiotte-Suchet and Probst, 1995), while models considering temperature and runoff provide lower values (-32 to 36%; (Dessert et al., 2003; Goll et al., 2014). Considering only temperature (new scaling equation developed for today's settings) results in only small differences in the global weathering fluxes of 10% compared to today, for areas with > 74 mm/a runoff. These calculations are based on highly specu-

C5

lative assumptions, like geographical distribution of active volcanic areas are as today. Specifically, we do not know the Holocene-equivalent area if using mid-Holocene as reference point for example. Therefore, we are not sure, what the reviewer wants us to do here. We do not understand how a "legacy" effect can be identified based on the available data and how this could be quantified. Therefore, we would like to keep this calculation out of the manuscript.

4. It would be helpful to provide detail of the water chemistry measurements or data involved in this study in the supplemental material. From the information provided, it is not possible for the reader to tell how variable the HCO₃⁻ measurements made were, which makes it hard to judge the estimates of CO₂ sequestration. While I appreciate that a full assessment of the chemical composition of the rivers in question is significantly outside the scope of the study, it would be helpful for clarity if the authors discussed the following points, either in main or supplemental text: ' How variable is the HCO₃ in the water? ' Are the rivers super-saturated with respect to calcite? This is a fairly important issue, as there is potential for secondary carbonate precipitation to form in the rivers and soils of a catchment, which means the final estimates of HCO₃ flux may be biased. ' What are the concentration – discharge relationships for HCO₃ in these rivers? If concentration is relatively high even at high discharge (i.e. are the rivers near-chemostatic? - e.g. Godsey et al. 2009, Hydrological Processes) then the largest storm events have the greatest importance for HCO₃ flux – and as a result, changes in climate across the Holocene transition (e.g. different storm frequency) may be relevant for the findings (see point 3 above). As I say above, I fully appreciate that data on these points may be lacking, and certainly addressing these points in full is outside the scope of this study – I would just suggest explaining how these issues may relate to your results, and what your assumptions are with regards to the river chemistry. This would really help the reader appreciate the results. A discussion of the assumptions could be incorporated into supplemental material.

We tried to address this important point here and put some sentence into the supple-

C6

ment:

For five areas water chemistry data are available (High Cascades, Japan, NE North America, SE Australia, South Africa and Tasmania), which allow saturation calculations, while for others either pH or major cations were not available. For these available data (103 catchments) the saturation index for calcite was calculated. In general, water samples are undersaturated with respect to calcite (77%). From the oversaturated samples 50% have values close to 0 and are below $SI=0.5$, which is also a typical value for rivers in limestone areas after areas where calcite is precipitated in case of a minimum oversaturation is reached due to degassing of CO_2 (Romero-Mujalli et al., 2018). The other 12 values are between 0.5 and 0.9 and locations are located in areas of South Africa or Australia.

In general, younger active areas have significant contributions of magmatic SO_4 or Cl , which shifts the saturation states normally further to lower negative values. We cannot conclude from the river data what happens in the aquifer system but reference the study of Jacobson et al. (2015), which quantified the contribution of trace calcite dissolution from basalt using Ca-isotope data.

5. This study is a useful addition to the study of Li et al. (2016), from which much (if not all?) of the data seems to be drawn. While I appreciate that the prior work is a published study, I think it is important that the authors explain their methodology in this publication too. For example, it would be useful to explain how alkalinity calculations were made, and some of the assumptions associated with the chemistry data; it would also be useful to summarise all of the uncertainty estimates made in that prior study in this study (see point 1). I notice that the Li et al. 2016 paper is open-access (much appreciated!), so I can appreciate that some researchers may feel it is sufficient to just cite the methods in the prior work. My personal preference is for as much of the relevant methodology for a given study to be described in that study as possible, but I leave this to the editor's discretion in this case.

C7

Li et al. (2016) calculated the alkalinity flux rates by multiplying the mean concentration of dissolved inorganic carbon (DIC) by the annual runoff. We included this explanation in the supplemental material. However, because the supplement is already very long, and the other data file is open access online, we would like to avoid replicating the data since the supplement is already rather long with over 40 pages, explaining the new data and calculations. Table S1 summarizes the hydrochemical data per volcanic area.

6. A small point, but one I feel worth mentioning – the HCO_3^- /reactivity figures in the supplementary material (lines 188-189) are a really useful accompaniment to Figure 1 in the main text, and I would suggest incorporating at least some of them into the main text. It really helped me understand the importance of temperature and runoff, and I think they're important enough to include. Even if you choose not to do so, it would be useful to ensure that the symbology in the figures corresponds to one another (i.e. red-blue points in the main text, red-green points in the supplement). I'd suggest using red-blue as in the main text, to avoid any issues with red-green colour blind readers.

We incorporated two of the figures in the main text and changed the colors to blue and red (now new: Figure 2a to 2d compare the relationships).

7. It may be useful to compare these findings to those relating to weathering in aging glacial moraines, to help contextualize the importance of aging? Your results are really intriguing, and provide impetus for research questions focused on e.g. weathering in lava flows of known age (via e.g. cosmo dating) and comparing to glacial moraines would be direct comparison.

Indeed, we included a reference from Taylor and Blum (1995), discussing this in the introduction, lines 44-45.

8. In line 40, you refer to 'geogenic nutrients'. I think this is a jargon term that many readers won't understand; I'd suggest defining this term before you use it. Additionally, I think this statement needs a citation to support it.

C8

This is a normal scientific use of common terms geo and genic. Geogenic means here derived from rock/lithosphere, comparable to the term anthropogenic.

9. In a couple of locations, you separate the arid and non-arid locations based on a rainfall total of >74mm per year – why was this figure chosen? It would be helpful to have some explanation as to this number.

As we explained in the text before 74 mm a-1 was the lowest runoff value of a volcanic field in the dataset of Li et al. (2016). We included an explanation in line 101-106 and show in the summary table of model comparison that the cutoff is necessary to avoid overestimation due to the temperature scaling law used.

10. I would suggest arranging references in chronological order where there are multiple citations in parentheses, e.g. Line 43 and other locations.

We agree with this point.

Typographical / Syntax points In general I found the paper to be well written and easy to read. There are a handful of places where the language is somewhat idiosyncratic, and I've tried to make suggestions where possible. As a general point I would recommend using the active voice rather than passive voice to improve readability, but that's probably a matter of personal preference.

Thank you very much.

Line 12: Consider being more specific than the word 'information' – perhaps describe which types of data you mean.

We rewrote this sentence.

Line 20: Instead of “from surface near material in the critical zone”, consider “from material in the shallow critical zone”

We agree and changed it correspondingly.

C9

Line 22: Remove comma after suggests

We deleted the comma.

Line 23: “Active basalt areas” is jargon – I'd suggest it's best to define what you mean in the main text and avoid using jargon terms in the abstract

We deleted “active”.

Line 30: “Basalt areas, despite its limited. . .” should be “Basalt areas, despite their limited. . .”. Also remove the 'the' before CO2.

We agree and changed it.

Line 39-40: Consider changing “The role of basalt weathering in the carbon cycle and its feedback strength in the climate system depends, besides the release of . . .” to “The importance of basalt weathering in the carbon cycle and the climate-weathering feedback loop depends in part on the release of geogenic nutrients but crucially on the amount of associated. . .”

We changed it to: “The role of basalt weathering in the carbon cycle and its feedback strength in the climate system depends, besides the release of geogenic nutrients, on the amount of associated CO2 consumption and related alkalinity fluxes.”

Line 59: Replace “However, the here suggested aging effect” with “However, the effect of aging on weathering rates from a volcanic system discussed here has not been evaluated.”

We replaced this part.

Line 68: Consider replacing “the fraction of the Holocene area on the total studied area” with “the proportion of total area occupied by Holocene lavas”

We changed this part.

Line 92-93: The word order and verb agreement in this sentence is somewhat unclear

C10

– I haven't suggested a revision since I don't want to mess with the meaning, but I'd suggest revising it to clarify what you mean.

We modified this part.

Line 100: Replace "For allowing comparison with" with "to allow for comparison with"

We replaced this.

Line 103: Replace 'reporting' with e.g. 'describing'

We agree and changed it.

Table 1: The first two columns in the table have no label? Please add a label to explain what these are.

We changed the labels of the table.

Line 152: Consider changing the phrase 'time stamp' – it isn't necessarily clear what you mean.

We replaced it by "time period".

Line 159: Replace 'Results' with "Our results". Also change 'considering' to 'exploring'

We changed this part.

Line 160: 'Displacement' – do you mean 'emplacement'?

We replaced it.

Line 164: I would suggest rephrasing to remove the comma.

We modified this part.

Final paragraph: Consider re-stating your key finding in the final paragraph.

We rewrote this part.

C11

Supplementary Material: Generally I found the supplementary material to be clear and helpful. Please ensure that uncertainty estimates are included where possible. I would also suggest checking with the editor as to whether the citations in the supplementary material will be indexed or not – it may be advisable to move them to the main text to ensure they get indexed.

Error estimates are now included in the supplemental material.

References: Amiotte-Suchet, P., and Probst, J. L.: A global model for present-day atmospheric/soil CO₂ consumption by chemical erosion of continental rocks (GEM-CO₂), *Tellus B*, 47, 273-280, 10.1034/j.1600-0889.47.issue1.23.x, 1995. Bluth, G. J., and Kump, L. R.: Lithologic and climatologic controls of river chemistry, *Geochimica et Cosmochimica Acta*, 58, 2341-2359, 1994. Dessert, C., Dupré, B., Gaillardet, J., François, L. M., and Allègre, C. J.: Basalt weathering laws and the impact of basalt weathering on the global carbon cycle, *Chemical Geology*, 202, 257-273, <http://dx.doi.org/10.1016/j.chemgeo.2002.10.001>, 2003. Ferrier, K. L., Riebe, C. S., and Jesse Hahm, W.: Testing for supply-limited and kinetic-limited chemical erosion in field measurements of regolith production and chemical depletion, *Geochemistry, Geophysics, Geosystems*, 17, 2270-2285, 2016. Goll, D. S., Moosdorf, N., Hartmann, J., and Brovkin, V.: Climate-driven changes in chemical weathering and associated phosphorus release since 1850: Implications for the land carbon balance, *Geophysical Research Letters*, 41, 3553-3558, 10.1002/2014GL059471, 2014. Jacobson, A. D., Grace Andrews, M., Lehn, G. O., and Holmden, C.: Silicate versus carbonate weathering in Iceland: New insights from Ca isotopes, *Earth and Planetary Science Letters*, 416, 132-142, <http://dx.doi.org/10.1016/j.epsl.2015.01.030>, 2015. Li, G., Hartmann, J., Derry, L. A., West, A. J., You, C.-F., Long, X., Zhan, T., Li, L., Li, G., Qiu, W., Li, T., Liu, L., Chen, Y., Ji, J., Zhao, L., and Chen, J.: Temperature dependence of basalt weathering, *Earth and Planetary Science Letters*, 443, 59-69, <http://dx.doi.org/10.1016/j.epsl.2016.03.015>, 2016. Romero-Mujalli, G., Hartmann, J., and Börker, J.: Temperature and CO₂ dependency of global carbonate weathering

C12

fluxes – Implications for future carbonate weathering research, *Chemical Geology*, <https://doi.org/10.1016/j.chemgeo.2018.08.010>, 2018. Taylor, A., and Blum, J. D.: Relation between soil age and silicate weathering rates determined from the chemical evolution of a glacial chronosequence, *Geology*, 23, 979-982, 1995. Wolff-Boenisch, D., Gislason, S. R., and Oelkers, E. H.: The effect of crystallinity on dissolution rates and CO₂ consumption capacity of silicates, *Geochimica et Cosmochimica Acta*, 70, 858-870, 2006.

Interactive comment on *Earth Surf. Dynam. Discuss.*, <https://doi.org/10.5194/esurf-2018-10>, 2018.