

***Interactive comment on* “Technical note: in situ measurement of flux and isotopic composition of CO₂ released during oxidative weathering of sedimentary rocks” by Guillaume Soulet et al.**

Anonymous Referee #2

Received and published: 3 April 2018

In their Technical Note entitled, “*in-situ* measurement of flux and isotopic composition of CO₂ released during oxidative weathering of sedimentary rocks”, Soulet et al. report the results of a “proof-of-concept” study aimed at determining the release rate of carbon dioxide from outcrops of weathered shales and partitioning this carbon dioxide between inorganic and organic sources using C isotopes. The authors clearly describe the design, implementation, and data analysis for their rock weathering chambers in such a way that I am confident that I, or any other researcher, could implement this technique elsewhere. While I ultimately think that this paper should be published in *Biogeosciences*, I have a few comments that I would like to see the authors address (described below).

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Firstly, I am confused by the distinction between a “direct” and “indirect” measure of a chemical weathering reaction. On Page 1 line 12, the authors imply that tracking reaction products (e.g., dissolved sulfate in rivers) is an indirect method. However, as carbon dioxide is also a reaction product, I do not see how their method is any more direct than measuring sulfate concentrations. Moreover, the relationship between the amount of product consumed (carbonate or organic carbon) and the amount of carbon dioxide release can be strongly modulated by the buffering capacity of natural waters. As a result, tracking carbon dioxide release may lead to a different assessment of the extent of reaction relative to a product that doesn’t partition into both the fluid and gas phase (e.g., sulfate ion). That being said, I do agree that their method provides a different perspective on weathering reactions than measuring the dissolved or solid phase chemistry of rivers. In particular, I think the Soulet et al. method averages over very different temporal and spatial scales (see below) that make it a nice complement to river based approaches. Perhaps some more clarity as to what the authors mean by direct versus indirect would be helpful.

The different stoichiometries for carbonate weathering by sulfuric acid (CWSA) presented as equations 2 and 3 have appeared elsewhere in the literature. However, I am not convinced that, in the context of this paper, there is a real distinction that can be made. The dissolution of one mole of calcium carbonate releases one mole of calcium ion (Ca^{2+}) and one mole of dissolved inorganic carbon (DIC; $2\text{H}^+ + \text{CaCO}_3 \rightarrow \text{Ca}^{2+} + \text{H}_2\text{CO}_3$), which is equivalent to 2 units of alkalinity per unit of DIC. The generation of sulfuric acid from pyrite oxidation can titrate these 2 units of alkalinity leading to a net reaction for CWSA that results in 0 units of alkalinity generation per unit of DIC generation ($\text{H}_2\text{SO}_4 + \text{CaCO}_3 \rightarrow \text{Ca}^{2+} + \text{SO}_4^{2-} + \text{H}_2\text{CO}_3$; equivalent to Equation 2 of Soulet et al.). Equation 3 of Soulet et al. predicts 1 unit of alkalinity generation per unit of DIC generation. In this way, it can be viewed as a 50/50 mixture of carbonate weathering by carbonic and sulfuric acids instead of a distinct pathway for CWSA.

Furthermore, the idea that Equation 2 reflects an “immediate” release of carbon diox-

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ide to the atmosphere misses the fact that the aqueous chemistry of weathering fluids will strongly modulate this flux. If there is sufficient generation of alkalinity from silicate weathering, the carbon dioxide produced from CWSA will partition more into the dissolved phase despite generally following the stoichiometry of Equation 2. Similarly, springs developed in carbonate terrains that lack abundant pyrite still degass carbon dioxide into the atmosphere despite the fact that the reaction for carbonate weathering by carbonic acid is often written as generating bicarbonate ion. In other words, without more constraints on the fluid composition, it difficult to directly relate the extent of an individual weathering reaction to changes in carbon dioxide concentrations (e.g., see Soetart et al. 2007 Maine Chemistry).

In general, this study lacks replication. While I do not think that this is a critical issue, it'd be worth acknowledging some of the limitations and/or adding more analysis where possible. For example, two chambers are shown in Figure 1C. Is there not two chamber's worth of data to show? Similarly, I am not sure if I found at what depth below the land surface the chamber was placed. Presumably this depth will have a large effect on the results. What depth was selected and why?

Page 2 Line 24 - There are many other papers that have used S (and O) isotope ratios to partition the sulfate budget including some that precede the Calmels et al. 2007 paper. For example:

* Cameron, Eion M., et al. "Isotopic and elemental hydrogeochemistry of a major river system: Fraser River, British Columbia, Canada." *Chemical geology* 122.1-4 (1995): 149-169.

* Spence, Jody, and Kevin Telmer. "The role of sulfur in chemical weathering and atmospheric CO₂ fluxes: evidence from major ions, $\delta^{13}\text{CDIC}$, and $\delta^{34}\text{SSO}_4$ in rivers of the Canadian Cordillera." *Geochimica et Cosmochimica Acta* 69.23 (2005): 5441-5458.

* Das, Anirban, Chuan-Hsiung Chung, and Chen-Feng You. "Disproportionately high

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rates of sulfide oxidation from mountainous river basins of Taiwan orogeny: Sulfur isotope evidence." *Geophysical Research Letters* 39.12 (2012).

* Turchyn, Alexandra V., et al. "Isotope evidence for secondary sulfide precipitation along the Marsyandi River, Nepal, Himalayas." *Earth and Planetary Science Letters* 374 (2013): 36-46.

* Hindshaw, Ruth S., et al. "Influence of glaciation on mechanisms of mineral weathering in two high Arctic catchments." *Chemical Geology* 420 (2016): 37-50.

* Torres, Mark A., et al. "The acid and alkalinity budgets of weathering in the Andes–Amazon system: Insights into the erosional control of global biogeochemical cycles." *Earth and Planetary Science Letters* 450 (2016): 381-391.

Page 6 Line 15 - I'd appreciate a few sentences that explain directly how V_{ch} and S were determined. I assume that the dimensions of the drill hole and the assumption that it was shaped as a perfect cylinder were used. However, this ignores the fact the the chamber walls are rough and not perfectly impervious. As a result, you are likely to get carbon dioxide from pores and cracks that intersect the chamber walls as alluded to on Page 9 Line 6. I'd appreciate some additional discussion on how this effects area-normalized estimates of carbon dioxide production rates.

Furthermore, are their constraints from porosity, permeability, grain-size, and/or fracture density measurements that can inform the "effective" volume that the chamber samples? Or, could the mass of CO_2 removed during the first few flushes inform this volume? Being able to determine an "effective" volume (as controlled by porosity, permeability, fracture density, grain size, etc.) would help others trying to replicate the methodology in determining if a site would be appropriate based on rock properties.

Page 8 Line 27 - How realistic is it that the chamber has such a high pO_2 ? My understanding of evidence from the oxygen isotopic composition of sulfate (e.g., Calmels et al. 2007), pyrite reactions fronts (Brantley et al. 2013 ESPL), and gas chemistry in

wells (Kim et al. 2014 GCA 2017 GCA) is that oxidative weathering takes place under relatively low pO_2 conditions for many systems. Does this mean that your method provides a maximum estimate of reaction rates?

Page 9 Line 9 - For the analysis of CO_2 fluxes, it is stated that 3-4 flushes are necessary to get the "true" flux determination. What statistical criteria was this determination based on? Similarly, what is the basis for designating 6 minutes as the amount of time to fit the carbon dioxide accumulation curve (Page 6 Line 11)? How do the calculated averages and standard deviations of CO_2 flux vary with measurement / integration time?

Page 9 Line 20 - I am not convinced that the difference between the 2 carbon isotopic samples reflects process and not fractionation. The analysis of carbon dioxide fluxes explicitly assumes that there are leaks in the system, which may induce fractionation. Similarly, two different methods were used for these samples. Finally, if the balance between oxidative reactions can vary daily, then why is the entire difference in the isotopic composition of CO_2 derived from the passive trapping method assumed to result from fractionation. In general, a better discussion of which isotopic signals are attributed to environmental process vs. sampling-induced fractionation and why would be helpful.

Page 10 Line 15 - **This is very interesting!**. In other words, the release ratio of inorganic to organic carbon determined by carbon isotope ratios is different than the relative abundances of inorganic and organic carbon present in the underlying rock. Specifically, the isotopic method "sees" more organic carbon than would be expected if one "unit" of rock was congruently weathered. Does this make sense with what is known about carbon and sulfur reaction fronts in weathering profiles?

Page 10 Line 21 - While I understand the motivation behind including section 3.3, I think that the different area normalization schemes between the chambers and river-based measurements precludes direct comparison. The area normalization in river systems

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refers to the catchment area. However, weathering takes place at depth within porous media such that the true surface area of reactive material that rivers source solutes from is likely poorly approximated by the catchment surface area. In the chamber experiments, the area normalization refers to the surface area of the chamber walls, which likely more closely approximates the true "reactive" surface area (see above). At the very least, this discrepancy between area normalization schemes should be discussed before generating comparisons between the different datasets. Depending on how reactive surface area scales with catchment area, the fact that the chamber-based estimates are close in magnitude to the river-based estimates may actually mean that there is a large discrepancy in the rates that they predict.

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2017-454>, 2017.

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