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Dear Editor Sébastien Fontaine,

Thank you for handling our manuscript. We have carefully considered and addressed both Reviewers suggestions and comments. These have resulted in revisions throughout the manuscript. In summary here, the main changes are:

- As prompted by Reviewer 1, and as you suggested, we have added the mathematical description of how longer-term passive trapping of CO₂ onto zeolite sieves can be related to shorter-term active measurements of CO₂ emissions. This text is based on our reply to reviews as published in *Biogeosciences Discussions*. We provide an overview of this in revised manuscript main text (Section 3.1) and the full details as an Appendix.
- 2) We now flag that the method we present is one approach to do this (final paragraph of Section 1), that it has not been replicated here and explain the challenges of doing so, before expanding on the resulting caveats (new paragraphs at the start of Section 3.3). These revisions address comments raised by both Reviewers as highlighted in your comments.
- 3) We now provide the CO₂ flux measurements in units of mgC m⁻² day⁻¹ at the first instance. This is intended to clarify to the reader that our fluxes represent those over a short period of time, allowing us to be more cautious when we compare these first CO₂ emission measurements to published work on oxidative weathering fluxes.
- 4) We provide an expanded discussion of the characteristics of the weathering zone and regolith production. We are more careful in our use of the 'direct' and 'indirect' terminology when referring to measurements of weathering fluxes (Reviewer 2).

We have upload our revised manuscript and we provide a word track-changes version here, so you can follow the nature and extent of the revisions.

Best regards,

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Dr. Guillaume Soulet on behalf of all co-authors

Soulet et al. response to Reviewer 1, for "Technical Note: *in situ* measurement of flux and isotopic composition of CO_2 released during oxidative weathering of sedimentary rocks"

We thank Camille Cros for reviewing our manuscript and for her helpful feedback. Below we address these comments, along with corresponding changes made to the manuscript text.

The main objective of this study is to present the results from a new method estimating the amount and origins of CO2 released during the weathering of sedimentary rocks. The released CO2 might have two origins: the degradation of limestone by sulphuric acid and the (geo)respiration of organic carbon. The method is based on a respiration chamber drilled directly on the rock. The released CO2 is measured by following the short-term (hours) accumulation of CO2 in the respiration chamber after lowering the pCO2 to near atmospheric pCO2. Three sources of CO2 could contribute to the accumulation of CO2 in the chamber: the atmospheric CO2 due to possible contaminations and/or leaks, carbonates and organic C. These tree sources were successfully separated by analyzing the 12C, 13C and 14C isotopic composition of released CO2. To this end, the CO2 was trapped by two systems of zeolite that actively (hours) or passively (months) trap the released CO2.

The study provides first estimations of CO2 emissions by oxidative weathering of sedimentary rocks, which were unfortunately not compared to another method. I would say this is the main limit of this study. The isotopic analysis of CO2 provided evidence of low contamination of sampled CO2 by atmospheric CO2, which validates the tightness of respiration chamber and method of CO2 sampling. It also allowed providing first estimation of contribution of the two mechanisms of weathering contributing to CO2 emissions (acid degradation of limestone versus organic C respiration), which could not be compared to another method. Although the main results could not be validated by using another independent method, these first estimations are useful and timely justifying a possible publication of this manuscript in BG. However, there are major drawbacks that deserve major revisions of the manuscript. First of all, the authors should acknowledge the fact that their method is not compared to other ones and is not replicated strongly limits conclusions about the accuracy, sensitivity and reproducibility of such method.

RE: A main concern of the reviewer is the lack of replication and comparison with other methods. To our knowledge, our study is the very first attempt to detect, measure, quantify, trap and partition the source of CO_2 emissions during weathering of sedimentary rocks in such settings where weathering and erosion rates are high. It is therefore not possible to compare our results to others. That is why, in the discussion section, we attempt to relate our results to other studies that have estimated the CO_2 flux at the scale of river catchments using geochemical proxies in river water. The fluxes are of the same order of magnitude, yet, they are obviously different. We provided some explanations for the discrepancies in the original manuscript.

In terms of replication, this is challenging. Our measurements are not set up in a laboratory where parameters could be controlled. Instead we are working directly in the field where environmental parameters vary with time and space. For example, a single chamber may be expected to provide different fluxes through time as a response to seasonal environmental changes (temperature, humidity). If one were to compare two different chambers, they are likely to yield different results at the same time because of local differences in the weathering substrate (caused by differences in the chemistry of the weathered rock, fracturing, connectivity, porosity, slope of the rock face...). Therefore, to take this method further, we would recommend a field set up which allows for repeated measurements over seasons, and one with multiple chambers to examine the importance of weathering substrate.

Accordingly, to acknowledge that one method is outlined in our manuscript (with active and passive CO_2 approaches), and so there is no comparison to an alternative method, we provide a summary of the above discussion in the revised version (revised manuscript section 3.3 P12 L15-27).

Why did you not compare the results obtained by several respiration chambers?

RE: Our Technical Note is a "proof-of-concept" study, of which the goal is to test and discuss the feasibility of directly measuring CO₂ emissions in sedimentary rocks during weathering and our ability to trap this CO₂ to

measure its isotopic composition and determine its source. We demonstrate here it is possible, and the results from only one chamber are needed for this purpose. Comparing the results obtained from several chambers would be very interesting but it is the focus of a very different study which, for instance, would aim to discuss the variability over space and time of the CO₂ emissions and source proportions.

Why did not compare your estimation of released CO2 based on short term measurement of CO2 accumulation in chamber with the amount of CO2 you trapped after several months of passive CO2 trapping by zeolite. This comparison could be a first way to evaluate your method of estimation. RE: See detailed answer below.

The method of partitioning of CO2 sources is absolutely not well introduced and explained. For example, P5 L3-6 you should explain that these three sources of CO2 (atmospheric, limestone, organic C) have different isotopic composition. And you should give some order of magnitude maybe. The system of equations (9) should be carefully explained, in particular all the variables must be defined (what does Fm mean?).

RE: Modified accordingly. We reword this section to make it clearer to the reader and all variables are now properly defined (see P8 L15-29).

(what does Fm mean?)

RE: Fm is a defined radiocarbon metric relating to the ¹⁴C-to-¹²C ratio measured in the sample normalized to that of a standard. The metric was already defined in the original manuscript and appropriate references cited (P7 L21-24).

Table 3 must include the isotopic composition of air of the site.

RE: The information was already available in Table 2 (sample DRA17-ATM-2703) although we acknowledge that it was not clearly stated. We moved this piece of information to Table 3 to make it clearer to the reader.

Results and discussions must be presented in distinct sections to clearly separate facts from their interpretations (and fit to the standard of BG).

RE: We feel that a section "Results and discussion" is fitting for this manuscript – results are presented in Tables 2, 3 and 4 and in Figure 3. Other technical Note papers at Biogeosciences have the same format (e.g., Yoon et al., 2016; Call et al., 2017). Instead we added subsections (see sections 3.2.1, 3.2.2 and 3.2.3) and modified the title of section 3.3 to make it more informative (now "3.3. First order comparison of the magnitude of our CO_2 fluxes with other methods estimating CO_2 fluxes"). An introductive paragraph is added to this section to highlight some limitations of our study and justify our comparison with other indirect methods.

To my opinion, the estimation of released CO2 by short-term measurement should be compared to the amount of CO2 trapped by zeolite. If this is not comparable, I expect detailed explanations of reasons.

RE: We assume that the Reviewer refers to any difference between the active trapping CO_2 flux measurements, and the mass of CO_2 on the passive trap (accumulated over ~3 months). We are grateful to Reviewer 1 for an opportunity to expand on this interesting question. Before answering, let's relate the passive trapping to short-term flux measurements.

Passive sampling is a practical application of the first Fick's law (Bertoni et al., 2004). In our case it is related to the diffusion (D) of CO₂ molecules in air caused by the gradient of CO₂ partial pressure between that of the chamber ($pCO_{2,Ch}$) and that of the zeolite trap ($pCO_{2,zeolite}$). This diffusion is defined for a period of time (Δ t) and is limited to the internal side of the tube linking the chamber to the zeolite trap, i.e. the diffusion path characterized by the tube length (L) and section area (a). It results in the trapping of a certain mass of carbon (mc) in the zeolite trap. In this case, first Fick's law may be written as follows:

$$pCO_{2,Ch} - pCO_{2,zeolite} = \frac{m_C}{\Delta t} \frac{L}{aD} \frac{RT}{PM_C} 10^6$$
(R1-1)

where R is the gas constant, T is temperature, P is pressure and M_c is the molar mass of carbon. Factor $10^6 \times RT/PM_c$ converts grams of carbon to cm³ of CO₂, and pCO₂ is here in ppm (cm³/m³). Note that the pCO_{2,zeolite} in the zeolite trap is equal to 0 ppm, since the zeolite is the CO₂ absorber. The equation thus reduces to:

$$pCO_{2,Ch} = \frac{m_C}{\Delta t} \frac{L}{aD} \frac{RT}{PM_C} 10^6$$
(R1-2)

Equation (R1-2) allows us to reconstruct the average partial pressure of CO_2 in the chamber $pCO_{2,Ch}$ during the sampling duration (Δt). Eq. R1-2 also indicates that the passive trapping is only directly linked to the partial pressure in the chamber over Δt . In other words, passive sampling is not related in a simple way to the flux of CO_2 entering the chamber.

The above text should partially answer the Reviewer's comment. However, we can try to go further.

Let's assume that the evolution of the pCO_2 in the chamber can be described (as we do in our manuscript for short-term flux measurements; see Eq. 7-8) following an exponential law (Pirk et al., 2016), we can express the $pCO_{2,ch}$ in the chamber based on other parameters:

$$pCO_{2,Ch} = \frac{1}{V_{Ch}} \left[\frac{q}{\lambda} \left(1 - \exp(-\lambda \Delta t) \right) + m_0 \right] \frac{RT}{PM_C} 10^6$$
(R1-3)

where V_{ch} is the volume of the chamber, q is the initial rate of carbon accumulation in the chamber, m₀ is the initial mass of carbon in the chamber (a value that corresponds to 400ppm of CO₂ in the volume of the chamber). λ , per unit of time, is the parameter that describes the diffusive processes responsible for the non-linear accumulation of carbon in the chamber (e.g. Fig. 3 in the manuscript). Note that Δt is very large (~3 months and thus ~150,000 minutes), thus exp($-\lambda\Delta t$)~0, and Equation R1-3 simplifies to:

$$pCO_{2,Ch} = \frac{1}{V_{Ch}} \left[\frac{q}{\lambda} + m_0 \right] \frac{RT}{PM_C} 10^6$$
(R1-4)

Note that Eq. R1-4 can be written only if we assume that the initial rate of carbon accumulating in the chamber (q) does not change over time. This is a very large assumption that we expect to be violated because q is unlikely to stay constant over time for various reasons including natural variability in CO_2 production and also changes in the diffusive processes when pCO_2 builds up in the chamber.

Equating Eq. R1-2 and Eq. R1-4 we obtain:

$$\frac{m_{C}}{\Delta t} \frac{L}{aD} \frac{RT}{PM_{C}} 10^{6} = \frac{1}{V_{Ch}} \left[\frac{q}{\lambda} + m_{0} \right] \frac{RT}{PM_{C}} 10^{6}$$
(R1-5)

Hence we can derive the rate at which carbon accumulates into the chamber based on the passive trapping parameters and λ , which is measured in the field over short time periods (during the active trapping – see Eq. 7-8 in the main text):

$$q = \lambda \left(\frac{m_{\rm C}}{\Delta t} \frac{L}{aD} V_{\rm Ch} - m_0\right) \tag{R1-6}$$

The flux can be inferred from the later equation using the internal surface area of the chamber (S_{Ch} ; same as S in the main text). If q was in gC/min, then the flux of carbon Q in gC/m²/year is:

$$Q = \lambda \left(\frac{m_c}{\Delta t} \frac{L}{aD} V_{Ch} - m_0\right) 525600 / S_{Ch}$$
(R1-7)

We can determine most of the parameters of equation (6) independently from the flux (Q or q), except for λ . For instance m_c, m₀, V_{ch}, S_{ch}, Δ t, a and L can be measured and D (diffusion of CO₂ in air) can be inferred/estimated from the literature. However, λ is determined using the short term flux measurements, <u>along with</u> the flux (i.e., Soulet et al. response to Reviewer 1, for "Technical Note: *in situ* measurement of flux and isotopic composition of CO₂ released during oxidative weathering of sedimentary rocks"

Q or q). Thus estimating the flux of CO_2 based on the rate of carbon trapped in the passive trap (m_c/ Δ t) is not independent from the short term CO_2 flux measurements. Thus comparing the fluxes obtained from the mass of carbon m_c recovered using the passive trap and using Eq. R1-7 and the direct measurement, is somewhat circular because they are not determined independently from each other.

For longer monitoring of field work sites, the mass of carbon trapped is still informative but only qualitatively since m_c or better else the rate carbon trapping per unit of time ($m_c/\Delta t$) are proportional to the flux of carbon Q to the chamber and the "leakiness" parameter λ . This is illustrated easily by writing equation Eq. R1-7 differently:

$$m_{C}/_{\Delta t} \propto Q/_{\lambda}$$
 (R1-8)

Interpretations of changes in $m_c/\Delta t$ are thus qualitative at this stage, and so beyond the scope of the present Technical Note.

In the revised version we added some discussion clarifying that, based on our current knowledge and measurements, passive traps can be used to provide qualitative constraint on mass fluxes over time (see revised manuscript P10 L1-8).

We propose that future work investigates whether the parameter λ can be characterised for a chamber independently from the active CO₂ flux measurements. If it can, the passive trap method can be used not only qualitatively (e.g. to look for changes in the mass of CO₂ collected on passive traps through time), but quantitatively (i.e. the monthly time-integrated CO₂ flux).

Title of section 3.3 is not clear and does not reflect the content. It seems that the objective of this section is to make a first comparison of estimation made by this study with published results from other sites.

RE: Indeed the objective of this section is to provide a first-order comparison between our results and other indirect river-catchment scale estimates of CO2 fluxes from around the world. We changed the title of this section to:

"3.3 First order comparison of the magnitude of our CO₂ fluxes with other methods estimating CO₂ fluxes"

If I understand well, your estimated amounts are far above the ones present in the literature. You should give some interpretations of these differences including the fact that your method has some bias that could lead to overestimations. First, the drilling can generate hyperactive surface by providing dust (small particles with high surface areas). Second, fresh surface is rich in organic C and limestone (because not previously exposed to O2). The CO2 may diffuse from pores of surrounding rock to chamber signifying that the surface of rock contributing to these estimations is larger than the sole surface of chamber.

RE: We partly replied to this comment in the Reviewer's detailed point P11L16. Regarding the additional specific points raised here by the reviewer:

- 1) <u>Hyper-reactive surface by providing dust while drilling.</u> The weathered marls in which we drilled are compact at depths greater than ~10cm (Mathys and Klotz, 2008; Osstwoud Wijdenes and Ergenzinger, 1998). But they are not extremely hard rock, and the chamber was drilled in about 1 or 2 minutes producing a coarse powder (that we actually needed to further grind to fine powder in the lab for our geochemical analyses). So we don't think that this powder was extremely reactive. Furthermore, before sealing the chambers the powder left inside the chamber was blown away using a compressed-air gun to minimize this phenomenon. We added a sentence in the revised manuscript stating we removed the powder before sealing (see revised manuscript P4 L19-20).
- 2) The rock surrounding the surface of the chamber contributes to the CO₂ flux. We agree that the rock surrounding the surface of the chamber contributes to the CO₂ flux, just because the weathering process naturally occurs at some depth within the rock face (probably in the regolith where gas can

penetrate through cracks). We realize that we might not have been clear enough about this point. What we call "rock" in the original manuscript should actually be referred to as the regolith which extends to up to ~20cm depth (Mathys and Klotz, 2008; Osstwoud Wijdenes and Ergenzinger, 1998; Maquaire et a., 2002). Thus when we drilled the chamber, we created a headspace, into an "ongoing-weathering" rock, in which CO2 can accumulate. This makes us able to measure a CO2 flux when we lower the pCO2 to that of the atmosphere. This net flux is the one we want to measure.

We added this information in the Study Area section (revised manuscript P4 L2-9) as well as in the Results and discussion section 3.1 (revised manuscript P9 L23-27).

Detailed comments:

P3L11: why did you set up these two methods of trapping? The idea must be introduced before.

RE: We dropped the mention of the two methods of trapping from the introduction. Furthermore the rationale behind using active and passive trapping was already explained in the method section of our original and revised manuscript.

P4L4. The rock-drill was used to dig a hole or a cylinder. This is only a part of the chamber.

RE: The rock-drill was used to drill directly into the rock/regolith a cylindrical chamber – 40cm-deep with an inner diameter of 2.9 cm. This is indeed only the headspace of the chamber. The rest of the chamber including how it is closed and sealed is described in the following lines (P4 L6-13 of the original manuscript)

P4L24-27 The drilling makes powder that can stay on the surface. I guess that dust is highly reactive compared to rock that, has already been exposed to weather and oxidation since many years. This should be stated and discussed somewhere, maybe in the discussion section.

RE: A relatively coarse powder is produced during drilling (with some coarse flakes). However, the rotating flute of the drill bit carries away most of the powder out of the hole/chamber. This allowed us to sample the powder to measure its organic and inorganic carbon contents and isotopes. Importantly, before sealing the chamber, the rock powder left in the chamber was blown away from the inside using a compressed air gun. This should minimize the impact of dust on the measured bulk CO₂ flux. A sentence stating this point was added in the revised version of our manuscript (P4 L19-20).

P6 L11-14 This text has no meaning for me, could you try to better explain? Concerning this section on the estimation of CO2 release, how did you manage the fact that released CO2 can accumulate in water present in the rock under the form of carbonates?

RE: Indeed, a part of the CO_2 could be dissolved in the interstitial water under the form H_2CO_3 to form carbonate anions, of which a part could be released to the Laval stream water (the stream that drains the catchment where we installed the chambers). However, we are actually interested in measuring the net flux of CO_2 to the atmosphere. Plumbing the whole system, i.e., quantifying the portion of CO_2 that is emitted to the atmosphere as well as that that is released to the Laval stream as the form of carbonates anions after redissolution or as a result of Eq. 3 is out of the scope of this study.

Equations 9. You must say that this system of three equations can calculate three unknowns: atmopsheric CO2, limestone originating CO2, organic C originating CO2. Define all variables. Results and discussions must be separated. That will clarify your results and explanations.

RE: These comments are related to comments already addressed above.

P8L18-20. Not necessary, the dissolution of CO₂ in water and formation of carbonates could lead to a non linear response.

Soulet et al. response to Reviewer 1, for "Technical Note: *in situ* measurement of flux and isotopic composition of CO₂ released during oxidative weathering of sedimentary rocks"

RE: We do agree in principle. However rock water content seems to be very low as it does not look wet and we don't see any water dripping at all. So we doubt that the process described here by the reviewer can impact significantly the changes in pCO2 we observe repeatedly during our sequences of CO2 monitoring. Instead we keep thinking that a host of diffusive processes (Pirk et al., 2016; Kutzbach et al., 2007) are most likely to explain these non-linear changes.

P9L1-2 This decrease could result from an exhaustion of CO2 of pores surrounding the chambers (at the beginning of measurement these pores contribute much to the accumulation of CO2 in the chamber and they become empty with time).

RE: We do agree. This is what we explained at P9 L6-9 in the original manuscript.

P9L17 I disagree. The amount of atmospheric CO2 is given by your system of equations (9) RE: The manuscript text was correct as written.

Third equation of the system of equations (9) is:

 $f_{Atm} \cdot Fm_{Atm} + f_{RockOC} \cdot Fm_{RockOC} + f_{Carb} \cdot Fm_{Carb} = Fm_{Chamber}$ (R1-8)

Since rock-derived organic carbon and the carbonates are devoid of radiocarbon (because they are very old – 160,000,000 years old, whereas 14 C is not measurable anymore after 50,000 years), hence their radiocarbon activity is 0. This implies that:

$Fm_{RockOC} = Fm_{Carb} = 0$	(R1-9)
Combining (R1-8) and (R1-9), it comes:	

$f_{Atm} = Fm_{Chamber} / Fm_{Atm} $ (R1-

Thus the relative amount of atmospheric CO₂ (f_{Atm}) is calculated as written at P9 L17 in our original manuscript.

P9L20 Cite Table 4

RE: Sentence at P9L20 refers to stable carbon isotopes reported in Table 2. So we guess that the reviewer meant Table 2 instead of Table 4. Accordingly we now cite Table 2 in the revised manuscript (P10 L19).

P10 L10-11 You should better explain why do you make a correction for atmospheric CO2 although this contribution was already considered in your system of equations? After reading Table 4, I understood but you should better explain in the text.

RE: Modified accordingly, we added the specific information (P11 L31 to P12 L3 in the revised version)

P10 L21-22 Change titles, they are not helpful for the understanding. RE: We already addressed this comment (see above)

P11 L3 You should add text to explain that your method must be compared with other (direct or indirect) methods on the same site.

RE: This is the aim of section 3.3 where we compare our method of direct CO2 flux measurements to other estimations of CO2 fluxes. In the revised version, we hope the title of section 3.3 is now clear enough.

P11 L5-9. The logical link between these sentences is not obvious.

RE: Modified accordingly, see P13 L18 in the revised manuscript: "*This statement is supported by the average anion* [...]"

P11L16 the numbers "19 to 37 gC m-2 yr-1" must be compared to "206 gC m-2 yr-1" of your study? The difference is enormous and deserves some explanations.

RE: We agree the difference is large. We already provided some explanations at P11L18-20 of the original manuscript.

We could have added that seasonality might be another explanation, as CO₂ flux during winter months flux could be very different than that during summer months as a results of changes in temperature and water content with impacts on the kinetics of rock weathering. We actually expect that the direct CO₂ flux measurements would change over the course of the year. The estimates using dissolved calcium in river average several months. So one cannot expect that our direct flux CO₂ measurements (for 1 discrete location on a given day) perfectly match the CO₂ flux estimate using Laval stream chemistry (0.8 km² averaging several months). Taken individually these CO₂ fluxes are not comparable. What we felt important was to show that in erosive environments both fluxes are high compared to other geochemical carbon transfers (e.g. silicate weathering CO₂ consumption).

We do not expand much on these explanations as our manuscript is a Technical Note. So this kind of discussion goes beyond the aim we set to our original manuscript. As Reviewer #2 notes, we explain a method that can now be installed more widely to explore these questions.

Figure 1: I do not see what pictures B and C bring to the story.

RE: We felt important to show a larger view of the field, as well as that the chamber are not drilled in soil horizons. In the case other reviewers would suggest that these pictures are superfluous, we will be happy to take them off of the paper.

Have you checked that all the materials you use, especially the products used to seal and make tight (e.g. expansive foam etc), does not emit CO2?

RE: We don't use expansive foam. Instead, we used outdoor silicon sealant (see P4L11 in the original manuscript). First we checked that the silicon sealant was not containing any curing agent like acetic acid, which may chemically alter the substrate around the hole. Second the flux measurements were performed when the sealant was fully dry (see P4L14). Flux measurements presented here were performed on March 2017, i.e., 3 months after we installed chamber H6 in December 2016. We are very confident that the sealant we use has no impact on our direct CO₂ flux measurements.

Soulet et al. response to Reviewer 2, for "Technical Note: *in situ* measurement of flux and isotopic composition of CO_2 released during oxidative weathering of sedimentary rocks".

We are grateful to Reviewer 2 for theses constructive comments and concerns. Below we address the comments raised and provide corresponding amendment done to the original manuscript.

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).

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.

RE: The words "direct" and "indirect" were used to refer to the way the flux of CO₂ emitted to the atmosphere during oxidative weathering of rocks has been measured/estimated in the literature. In other words, whether CO₂ was being tracked directly, or by another product of the reaction (e.g. Re, or SO₄) which is what we meant by 'indirectly'. However, we acknowledge that in two occurrences it was not clearly stated and agree with some of the reviewer's comments above. We have thus modified the manuscript accordingly (see P1 L11 and P2 L19 in the revised manuscript).

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; $2H^+ + CaCO_3 \rightarrow Ca^{2+} + H_2CO_3$), 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 ($CaCO_3 + H_2SO_4 \rightarrow Ca^{2+} + SO_4^{2-} + H_2CO_3$; 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.

RE: We agree with Reviewer 2. However, we make the distinction between these two pathways in our manuscript in order to link our work to a wider problem that includes the impact of oxidative weathering of rocks (including CWSA) on the CO₂ concentration of the atmosphere over different timescales. We feel it can be better understood for a wider community using these two (and too) simple equations: Equation 2 implying the "immediate" release of CO₂ to the atmosphere, and Equation 3 implying the release of CO₂ over the timescale of 10,000 to 1,000,000 years. Depending on the fluxes involved, these pathways could thus impact climate over different timescales.

Furthermore, the idea that Equation 2 reflects an "immediate" release of carbon dioxide 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).

RE: In the context of our study, "immediately" has to be compared to the timescales of 10,000 to 1,000,000 years. We acknowledge that in details aqueous chemistry of weathering fluids may modulate the CO_2 flux, but from a geological point of view (10⁴ to 10⁶ year), this flux of CO_2 is an "immediate" response to oxidative weathering of rocks.

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?

RE: We do acknowledge that our methodology lacks replication, that's why we attempt comparing our results to other methods on other catchments despite issues of scales (see below). However, we are working in natural settings and we expect changes in the CO₂ flux and isotopes in response to seasonal physical-meteorological changes in the catchment area. So we do not expect to find the exact same results for a single chamber over time, and for different chambers at the same time. Please also see our reply to Reviewer #1.

Based on both reviewers' comments we added a section regarding the limitation of our methodology (section 3.3 in the revised manuscript P12 L15-27).

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?

RE: We drilled the chambers on bare rock outcrops, and in places where we could not see roots (see Fig. 4). These outcrops make up 68% of the surface area of the catchment (Mathys et al., 2003; Cras et al., 2007) and are key parts of the landscape contributing to weathering, solute production (Cras et al., 2007) and sediment production (Mathys et al., 2003; Graz et al., 2012). These pieces of information were added in section 2.1 of the revised manuscript (P3 L25-32 and P4 L1-9).

Then, chambers are in the unsaturated zone, and the depth at which they were drilled depended on the accessibility in the field. Chamber H6 was drilled at ~2 meters above the Laval stream (P8 L3 in the revised manuscript).

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 riversystem: 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, δ 13CDIC, and δ 34SSO4 in rivers of the Canadian Cordillera." Geochimica et Cosmochimica Acta 69.23 (2005): 54415458.
- * Das, Anirban, Chuan-Hsiung Chung, and Chen-Feng You. "Disproportionately high 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 weather-ing 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.

RE: Thanks. We added Spence and Telmer (2005) and Hindshaw et al. (2016) in the revised version of our manuscript.

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 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.

RE: V_{Ch} and S were indeed determined assuming that the drilled hole is a perfect cylinder. We do agree that CO_2 from a certain thickness around the drilled hole contributes overwhelmingly (compared to the CO_2 flux produced at the rock-chamber interface) to the flux we measure.

However, it has to be noticed that we want to provide the community with a flux of CO_2 emitted from the rock natural surface to the atmosphere. This flux includes the CO_2 produced at the rock-atmosphere interface and the CO_2 produced over a certain thickness from the weathered rock. In Draix, the thickness of the regolith is up to 10 to 20cm thick (Oostwoud Wijdenes & Ergenzinger, 1998; Mathys and Klotz, 2008). This means that the CO_2 flux from the rock to the atmosphere is produced over a thickness of 10 to 20cm. Thus, when we drill a 40cm-long hole, rather than creating a new weathering surface at the rock-chamber interface, we instead create a headspace that makes us able to measure a realistic flux of CO_2 from the rock to the atmosphere when we lower the p CO_2 to ~400ppm (atmospheric p CO_2).

We do agree that it was not clearly stated in the paper. We added some lines to state this point in the section 3.1 P9 L23-27 in the revised manuscript.

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 CO₂ 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.

RE: There are some estimates of the rock properties for the Laval Catchment (Mathys et al., 2003; Oostwoud Wijdenes & Ergenzinger, 1998; Traveletti et al., 2002). These suggest i) the upper ~3 cm are loose material composed of mm-to-cm fragments of marls, ii) from ~3 to ~10cm is the regolith of marl more or less fragmented, iii) from~10 to 20 cm is the compact lower regolith keeping the marl structure but not its cohesion, and iv) the bedrock (unweathered marl). The porosity has been determined to be 0.17-0.23 (Traveletti et al., 2012). We have added these details to the study area part of the manuscript to help others seeking to replicate the methodology (Section 2.1 P4 L1-9).

However, what matters for the "effective" volume is the connected porosity and gas permeability which is, as the reviewer states, is probably linked closely to the fracture density. There are no measurements of this parameter at the field site and so we cannot use the mass of CO₂ removed during the first flushes to inform us of this "effective" volume.

The purpose of our Technical Note is to show that one can measure reliable CO_2 flux to the atmosphere using a cylindrical chamber and trap enough CO_2 in the field to partition its source through its isotope composition (notably using ¹⁴C which requires larger volumes of CO_2 to be collected). The controls on this flux (of which rock properties and connected porosity are likely to be one) cannot be assessed without more measurements at a range of chambers, and at a range of field sites.

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?

RE: Weathering occurs not only at the atmosphere-rock interface but over at least a certain thickness into the rock (Petsch et al., 2000; Bolton et al., 2006). Nevertheless, at the atmosphere-rock interface pO_2 is that of the atmosphere. From the chamber point of view, a pO_2 of that of the atmosphere replicates what occurs when the rock is exposed to the atmosphere while pO_2 probably decreases in depth in the rock.

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It has to be noticed that our field site is not comparable to those described in the citations provided by Reviewer 2. In the suggested studies, erosion is much lower, leading to a very thick weathering front of 20 m or more (e.g., Brantley et al., 2013). In Draix – our field study – erosion removes 1cm of rock in average per year but it can be more. So the weathering front is probably far less thick, and pO_2 higher.

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?

RE: When the flux measured vs. number of repeats is examined (Figure R1), one observes a decrease in the flux that reaches steady values after 3 to 4 repeats, while statistically the last four are indistinguishable within 2σ . We are deliberately vague in our manuscript as this feature can change depending on the chamber and flux. In practice, the number of repeats on which flux is averaged has to be adapted based on the results observed.



Figure R1: Evolution of the measured flux with the number of repeats (grey filled squares, error bars are 2σ). Dashed line is the averaged flux over the last 4 repeats (257±8 gC/m²/yr) and yellow bar represents the 2σ-domain of the averaged flux.

Regarding the window for the flux measurements. If we pick 1 to 8 minutes of fitting, the results all agree within 2 sigma (Figure R-2).

The fitting window has to be specified and in our case, 6 mins were chosen as a trade-off. In our manuscript, we present a series of active trapping for which we left the chamber replenish with CO₂ for more than 6 mins. However, when on field, we are not necessarily trapping CO₂. Instead we are sometimes only measuring fluxes. In these cases, for logistical reasons mainly related to the time we can spend in the field daily, we are monitoring over shorter periods of 7 minutes. Thus fitting over 6 mins was sensible. This parameter can be modified as soon as it is specified. For example, Pirk et al (2016) chose 3-minutes fitting windows. The starting point of the fitting window may also impact slightly the results, although providing similar results within 2 sigma, if it is set to pCO₂ close to atmospheric values.

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Figure R2: Evolution of the average flux (over the last 4 repeats) with changing fitting time windows from 1 to 8 minutes (grey filled circles, error bars are 2σ). All data agree within 2σ. Please, note that scale of y-axis is different from Figure R1.

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 CO₂ 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.

RE: Previous studies when developing the passive method quantified an isotopic fractionation (Garnett et al., 2009; Garnett and Hardie, 2009; Garnett and Hartley, 2010). In contrast, the pump/active method doesn't fractionate, as shown by e.g. Hardie et al 2005.

We agree that our discussion about fractionation was a bit short. We expanded this discussion and highlighted potential limits but also benefits of using the passive and active sampling methods.

Please note that we changed the 3.5 ± 0.45 ‰ fractionation values (based on merging values provided in Garnett et al., 2009; Garnett and Hardie, 2009) by the now accepted value of 4.2 ± 0.3 ‰ (Garnett and Hartley, 2010) based on a laboratory assessment. This value is indistinguishable from the value obtained in Garnett and Hardie (2009) of 4.0 ± 0.2 ‰. The new applied value minimally changes the source partitioning results and does not changes our interpretations.

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?

RE: Once again, in Draix the weathering profile is probably thin (several decimeters) compared to other weathering profiles published (several meters; e.g., Brantley et al., 2013). At this stage, we reiterate the explanation we provided in the original version of our manuscript (P10 L18-20). The dissolution of carbonate depending on the oxidation of sulphides, it is therefore likely that it only occurs locally where sulphides are

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concentrated. In comparison the oxidation of organic carbon appears to occur homogeneously in the rock mass. We agree it is interesting and worthy of future study.

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 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.

RE: We somewhat agree and have added discussion to the revised version which relates to the referee's comment. This is a common issue when referring to element fluxes per unit of surface area. With more CO₂ flux measurements, alongside solute-based weathering estimates, we will be in a better position to probe these differences in more detail.

Technical note: *in situ* measurement of flux and isotopic composition of CO₂ released during oxidative weathering of sedimentary rocks

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Abstract. Oxidative weathering of sedimentary rocks can release carbon dioxide (CO₂) to the atmosphere and is an important

- 10 natural CO₂ emission. Two mechanisms operate the oxidation of sedimentary organic matter and the dissolution of carbonate minerals by sulphuric acid. It has proved difficult to directly measure the rates at which CO₂ is emitted in response to of these weathering processes in the field, with previous work generally using indirect methods which track the dissolved products of these reactions in rivers. Here we design a chamber method to directly measure CO₂ production during the oxidative weathering of shale bedrock, which can be applied in erosive environments where rocks are exposed frequently to the atmosphere. The
- 15 chamber is drilled directly into the rock face and has a high surface area to volume ratio which benefits measurement of CO₂ <u>fluxes. It is -and is a relatively low cost method toand provides a long-lived chamber (several months or more), oxygenated</u> environment in contact with a surface area of potential reactant. To partition the measured CO₂ fluxes and the source of CO₂, we use zeolite molecular sieves to trap CO₂ 'actively' (over several hours) or 'passively' (over a period of months). The approaches produce comparable results, with the trapped CO₂ having a <u>radiocarbon activity (Fraction modern, Fm) fraction</u>
- 20 modern ranging from $\underline{Fm} = 0.05$ to $\underline{Fm} = 0.06$ and demonstrating relatively little contamination from local atmospheric CO₂ (fraction modern of $\underline{Fm} = 1.01$). We use stable <u>carbon isotopes</u> of the trapped CO₂ to partition between an organic and inorganic carbon source. The measured fluxes of rock-derived organic matter oxidation (<u>171±5 mgC.m⁻².day⁴</u>) and carbonate dissolution by sulphuric acid (<u>534±17 mgC.m⁻².day⁻¹</u>) from a single chamber were high when compared to the annual flux estimates derived from using dissolved river chemistry in rivers around the world. The high oxidative weathering fluxes are , but
- 25 consistent with the high erosion rate of the study region $(of \sim 5 \text{ mm yr}^4)$. We propose our in situ method has the potential to be more widely deployed to directly measure CO₂ fluxes during the oxidative weathering of sedimentary rocks, allowing for the spatial and temporal variability in these fluxes to be determined.

1 Introduction

The stock of carbon contained within sedimentary rocks is vast, with $\sim 1.25 \times 10^7$ PgC contained within organic matter and $\sim 6.53 \times 10^7$ PgC as carbonate minerals (Sundquist and Visser, 2005). If these rocks are exposed to Earth's oxygenated surface,

Commented [SGS1]: We now provide the CO2 flux measurements in units of mgC/m2/day at the first instance. This is intended to clarify to the reader that our fluxes represent those over a short period of time, allowing us to be more cautious when we compare these first CO2 emission measurements to published work on oxidative weathering fluxes.



for instance during rock uplift, erosion and exhumation, oxidative weathering can result in a release of carbon dioxide (CO_2) from the lithosphere to the atmosphere (Petsch et al., 2000). There are two main processes to consider: i) the oxidation of rockderived organic carbon (Berner and Canfield, 1989; Petsch, 2014), which can be expressed by the (geo)respiration of organic matter:

$$5 \quad CH_2 0 + 0_2 \to CO_2 + H_2 0 \tag{1}$$

and ii) the oxidation of sulphide minerals (e.g., pyrite) which produces sulphuric acid, which can chemically weather carbonate minerals and release CO_2 (Calmels et al., 2007; Li et al., 2008; Torres et al., 2014) by the reaction:

$$CaCO_3 + H_2SO_4 \to CO_2 + H_2O + Ca^{2+} + SO_4^{2-}$$
⁽²⁾

or

 $10 \quad 2CaCO_3 + H_2SO_4 \to 2Ca^{2+} + 2HCO_3^- + SO_4^{2-} \to CaCO_3 + CO_2 + H_2O + Ca^{2+} + SO_4^{2-}$ (3)

In the case of Eq. (1) and Eq. (2), CO_2 is released to the atmosphere <u>at the site of chemical weathering</u>"immediately". In the case of Eq. (3), CO_2 is released to the atmosphere over a timescale equivalent to that of the precipitation of carbonate in the ocean (~10⁴ to 10⁶ years; Berner and Berner, 2012).

- The fluxes of carbon transferred to the atmosphere in response to both oxidative weathering processes are thought to be as 15 large as that released by volcanic degassing, but the absolute fluxes remain uncertain (Li et al., 2008; Petsch, 2014). As such, both processes act to govern the levels of atmospheric CO₂ and O₂, and hence Earth's climate over geological timescales (Berner and Canfield, 1989; Torres et al., 2014). The oxidation of rock-derived organic carbon may also contribute to modern biological cycles, especially rock substrate that is rich in organic carbon (Bardgett et al., 2007; Copard et al., 2007; Keller and Bacon, 1998; Petsch et al., 2001). Various approaches have been adopted to better quantify these major geological CO₂ sources.
- 20 These include the use of geochemical proxies in rivers, which indirectly track the CO₂ emissions released-from the oxidative weathering of sedimentary rocks at the catchment-scale. For instance, the trace element rhenium has been used to compare relative rates of rock-derived organic carbon oxidation (Jaffe et al., 2002) and estimate the corresponding fluxes of CO₂ across river catchments (Dalai et al., 2002; Hilton et al., 2014; Horan et al., 2017). Another approach has been to measure the loss of radiocarbon-depleted organic matter in river sediments during their transfer across the floodplains of large river basins
- 25 (Bouchez et al., 2010; Galy et al., 2008). In the case of sulphuric acid-weathering of carbonate minerals, the dissolved sulphate flux can be informative if the source of SO₄²⁻ has been assessed using sulphur and oxygen isotopes (Calmels et al., 2007; <u>Hindshaw et al., 2016; Spence and Telmer, 2005</u>) and/or using the dissolved inorganic carbon flux and its <u>stable carbon isotope</u> δ¹³C-composition (δ¹³C) (Galy and France-Lanord, 1999; Li et al., 2008; <u>Spence and Telmer, 2005</u>).

It should be possible to directly measure the flux of CO_2 emanating from sedimentary rocks in response to oxidative weathering. Keller and Bacon (1998) explored such an approach in a 7 m deep soil on till, suggesting geo-respiration of Cretaceous age organic matter was an important source of CO_2 at depth. However, this research has not to our knowledge been replicated, nor applied in erosive landscapes where sedimentary rocks are frequently exposed to weathering by erosion processes (Blair et al., 2003; Hilton et al., 2011). In these locations, oxidative weathering fluxes are thought to be very high (Calmels et al., 2007; Hilton et al., 2014; Petsch et al., 2000). One of the challenges of tracking CO_2 directly is that flux

measurements must be combined with the isotopic composition (¹²C, ¹³C and ¹⁴C) of the CO₂ (Keller and Bacon, 1998). Only with that information can the measured CO₂ flux be partitioned into the component derived from the oxidation of rock-derived carbon and that derived from the dissolution of carbonate (in addition to inputs from the modern plant and soil biosphere, and atmospheric inputs).

The objective of this paper is to provide a detailed proof of concept study of methods we have designed which can: (1) make direct measurements of the flux of CO₂ released during the oxidative weathering of sedimentary rocks; and (2) trap the CO₂ produced during weathering in order to measure its isotope composition, and partition the source of the CO₂ flux between rock-derived organic carbon and carbonate. Here we outline <u>one approach to address these research gaps which adapts a the</u>

15 chamber-based method to measure CO₂ fluxes. We ,- and provide the first examples of its application of active and passive methods to trap CO₂ and use its-the isotope composition to directly quantify the <u>fluxesrate</u> of <u>CO₂ from oxidative</u> weathering reactions.

2 Methods

5

2.1 Study area

- 20 The study location is within the Laval catchment, part of the IRSTEA Draix Bléone Experimental Observatory and the Réseau des Bassins Versants network, located near the town of Draix, Alpes de Haute Provence, France. The small catchment (0.86 km²) is heavily instrumented, with continuous monitoring of rainfall, river water discharge, river solid load transport, total dissolved fluxes and physical erosion rates over the last four decades (Cras et al., 2007; Mathys et al., 2003). These measurements provide hydrodynamic and geomorphic context for any studies of oxidative weathering. The lithology of the
- 25 catchment is composed of <u>black Jurassic marine marls (from the Bajocian to the Callovo-Oxfordian marlsstages)</u>, which contain inorganic carbon and organic matter (Graz et al., 2012). Sulphide minerals are widespread as disseminated pyrite and veins which outcrop in the catchment (Cras et al., 2007). The rock-strength, climate and geomorphic setting combine to produce a badland-type morphology with very steep and dissected slopes.
- Erosion rates are very high, with sediment export fluxes of 11,200 tons.km⁻².yr⁻¹ on average during the period 1985 to 2005
 30 AD (with a minimum of 4,400 tons.km⁻².yr⁻¹ in 1989 and a maximum of 21,100 tons.km⁻².yr⁻¹ in 1992) (Graz et al., 2012; Mathys et al., 2003). Assuming a regolith bulk density of ~1 to 1.5 tons.m⁻³ (Mathys and Klotz, 2008; Oostwoud Wijdenes and Ergenzinger, 1998), this equates to a physical erosion rate of ~7 to 10 mm.yr⁻¹ on average, but that can reach maximum

values of 20 to 14 mm.yr⁻¹. These features limit the development of soils and bare rock outcrops represent 68% of the catchment surface area (i.e., 0.58 km²) (Cras et al., 2007; Mathys et al., 2003). As a result, it is easy to find regolith and rock surfaces that are devoid of soils and roots, and where sedimentary rocks are directly exposed to the oxygen-rich atmosphere.⁵ These are key parts of the landscape contributing to weathering, solute production (Cras et al., 2007) and sediment production (Graz et al.,

- 5 2012; Mathys et al., 2003; Oostwoud Wijdenes and Ergenzinger, 1998). Bare rock outcrops are characterized by the development of weathered marls and regolith. Regolith typically extends at least to ~20 cm with the following characteristics:
 i) the upper ~3 cm are-is loose detrital cover composed of mm-to-cm fragments of marls, ii) from ~3 to ~10cm is the loosened upper regolith which is somewhat fragmented, iii) from ~10 to 20 cm is the compact lower regolith which retains the marl structure but not its cohesion, and iv) at depths more than ~20cm is the marl bedrock (unweathered marl) (Maquaire et al.,
- 10 2002; Mathys and Klotz, 2008; Oostwoud Wijdenes and Ergenzinger, 1998). Lateral variation in the regolith thickness exists with larger thicknesses on crests, intermediate in gullies and minimal in talwegs (Maquaire et al., 2002). Marl bedrock porosity ranges between 0.17 and 0.23 (Traveletti et al., 2012). Erosion rates are very high, with sediment export fluxes of 11,200 tons.km⁻².yr⁺¹ on average during the period 1985 to 2005 AD (with a minimum of 4,400 tons.km⁻².yr⁺¹ in 1989 and a maximum of 21,100 tons.km⁻².yr⁺¹ in 1992) (Graz et al., 2012; Mathys et al., 2003). Assuming an average rock regolith bulk density of
- 15 ~2.21 to 1.5 tons. m³-(Oostwoud-Wijdenes and Ergenzinger, 1998; Mathys and Klotz, 2003), this equates to a physical crosion rate of ~5 10 to 7 mm. yr⁴-ion average, but that can reach maximum values of 20 to 14 mm.yr⁴. These features limit the development of soils, typically 20-to-30-cm thick where they are present at all. As a result, it is easy to find regolith and rock surfaces that are devoid of soils and roots, and where sedimentary rocks are directly exposed to the oxygen-rich atmosphere.

2.2 Natural oxidation and CO2 accumulation chambers

- 20 In order to measure the flux of CO₂ produced by oxidative weathering of sedimentary rocks, and accumulate enough CO₂ to perform-<u>stable</u> carbon isotope <u>and radiocarbon</u> measurements, we use accumulation chambers (e.g., Billett et al., 2006; Hardie et al., 2005). These have been extensively used to measure soil respiration (e.g., Hahn et al., 2006; Hardie et al., 2005), CO₂ evasion by streams and rivers (e.g., Billett et al., 2006; Borges et al., 2004), but have not yet been used to examine rock-atmosphere interactions. Because most fine-grained sedimentary rocks have a degree of competency, accumulation chambers
- 25 can be made by directly drilling into the rock. Here we use a rock-drill to make 40 cm-long chambers with an inner diameter of 29 mm. Our aim was to minimise the volume of the chamber while maximizing the surface of exchange with the surrounding rock.

The rock powder left inside the chamber after its drilling was blown away using a compressed-air gun in order to minimize

- the presence of potentially reactive dust. Then, After after measuring the dimensions of the chamber, its entrance is fitted with a small PVC tube (~3_cm-diameter, ~3_cm-long), which allows a tight seal with an inserted rubber stopper containing two holes. Two Pyrex® tubes (ID=3.4_mm and OD=5_mm; one of 12_cm-long and one of 7_cm-long) are inserted through the rubber stopper. The differential length is to improve airflow in the chamber while in operation. The sections of the Pyrex® tubes sticking out of the chamber are fitted with Tygon® tubing (E-3603; Saint Gobin, France). To isolate the accumulation
 - 4

chamber from the atmosphere as best as possible, the Tygon® tubing is sealed with WeLock® clips (Scandinavia Direct Ltd, UK) and silicone sealant (Unibond® Outdoor) is placed around the entrance of the chamber (the 3cm-diameter PVC tubing and the rubber stopper) (Figure 1). The newly installed chamber is left for ~2 days to allow the sealant to fully dry. Here we acknowledge that a perfect seal is impossible, due to the natural rock fracturing around the chamber. Table 1 summarises the dimensions of an example chamber drilled and sealed in the field on 13th December 2016.

- Drilling results in the formation of an oxidative weathering zone by introducesing an oxygen-rich atmosphere in the chamber and surrounding marl regolith and bedrock (similar to outcropping marls exposed to the atmosphere). If gaseous O_2 is consumed (e.g. by Eq. (1)), this would create a gradient in the partial pressure of O_2 (p O_2) whereby the atmosphere surrounding the rock and chamber is of higher p O_2 . Given the natural porosity and permeability of the shale bedrock, any diffusion of O_2
- 10 is likely to be into the chamber. This should act continuously to fuel the chamber with oxygen. In contrast, if CO₂ is produced inside the chamber (by Eq. (1) and Eq. (2)) then the partial pressure of CO₂ (pCO₂) will exceed that of the atmosphere. The result is that for chambers where oxidative weathering is occurring, the ingress of and 'contamination' by atmospheric CO₂ should be minimal, and there should be a supply of O₂ for reactions. These inferences can be tested using a pO₂ probe and by trapping CO₂ and measuring its isotope composition.
- 15 In this example we aimed to measure oxidation of sedimentary rocks, and intended to minimise the role of CO₂ produced by root respiration. Therefore, the chambers were drilled on cleared rock surface, devoid of visible roots. The rock powder produced when drilling the chambers was collected, freeze-dried and grinded in the laboratory to fine powder for measurement of its organic-inorganic carbon content and its isotopic composition.

2.3 CO₂ flux measurements

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- 20 A closed-loop CO₂ sampling system similar to the molecular sieve sampling system (MS³) described in Hardie et al. (2005) was used for CO₂ flux measurements and CO₂ sampling (Figure 1). The system incorporated the following components: an air filter, a water trap (cartridge filled with magnesium perchlorate), a portable infrared gas analyser (IRGA) equipped with an internal air pump, calibrated to a pCO₂ range of 0 to 5000 ppmv and installed with an pO₂ probe (EGM-5, PP Systems, <u>US</u>), a CO₂ scrub (cartridge filled with soda lime), a bypass, and a set of WeLock® clips that allows the air flow to be diverted through
- 25 the bypass or the CO₂ scrubber cartridge. Optionally a zeolite molecular sieve sampling cartridge can be inserted in the line (see next section).

Before each CO₂ flux measurement, the Tygon[®] tubes exiting the chamber were fitted with autoshutoff Quick CouplingsTM (Colder Products Company, USA), and the CO₂ contained within the sampling system is removed using the CO₂ scrubber cartridge. When no CO₂ is left in the sampling system (as indicated by the IRGA), the air flow is diverted through the bypass,

30 and the system connected to the chamber (Figure 2). The use of the auto-shutoff couplings prevents atmospheric contamination at the moment of connection to the chamber. Then, pCO₂ in the chamber is lowered to near atmospheric pCO₂ by guiding the air flow through the CO₂ scrubber cartridge. We let the CO₂ accumulate in the chamber for several minutes (typically 10 minutes) by guiding the air flow through the bypass (Figure 2). This operation can be repeated several times to provide multiple

measurements of CO_2 flux over a period of hours (Figure 3). The CO_2 evolution in the chamber typically shows a curvature, the curve flattening with time and higher concentration (Figure 3). In order to calculate the CO_2 flux, we first convert the p CO_2 measurements into the mass of carbon contained in the chamber:

$$m = \frac{pCO_2}{10^6} \cdot V \cdot A \tag{4}$$

5 where m is the mass of carbon in the chamber (in mgC), pCO₂ the concentration of CO₂ in the chamber in ppm (cm³.m⁻³), V is the total volume (cm³) i.e., the sum of the volume of the chamber ($V_{CH}V_{Ch}$) and the volume of the CO₂ sampling system (V_L) when air flows through the bypass. Factor A converts centimetres cubed of CO₂ into milligrams of carbon, depending on temperature and pressure following the ideal gas law:

$$A = \frac{P \cdot M_{\rm C}}{R \cdot T} \cdot 10^{-3}$$
(5)

10 where P is the pressure (Pa) as measured by the IRGA, M_C is the molar mass of carbon (g.mol⁻¹), R is the gas constant (m³.Pa.K⁻¹.mol⁻¹) and T the temperature (K) in the chamber. Then the rate (q in mgC.min⁻¹) at which carbon accumulates in the chamber is calculated using an exponential model (described below; Pirk et al., 2016) and converted into a flux of carbon (Q in mgC.m⁻².dayy+⁻¹) emitted to the atmosphere under the form of CO₂ using:

$$Q = 1440 \, q/S \frac{q}{s} \cdot 525.6$$
(6)

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where, $\frac{525.61440}{10}$ converts mgC.min⁻¹ into mgC.day⁻¹yr⁻¹, and S (m²) is the inner surface area of the chamber exchanging with the surrounding rock. To calculate the rate of accumulation of carbon (q) in the chamber we use the exponential model described by Pirk et al. (2016):

$$\frac{\dim(t)}{t} = q - \lambda(m(t) - m_0) \tag{7}$$

20 where $\frac{dm(t)}{dt}$ is the carbon mass change in the chamber with time. Parameter m_0 is the mass of carbon in the chamber at the beginning of the CO₂ accumulation and that should be close to the mass of carbon in the chamber at atmospheric pCO₂. The constant λ (in units of time⁻¹, here in min⁻¹) describes the sum of all processes which are proportional to the carbon mass difference $\Delta m(t) = m(t) - m_0$ and is responsible for the curvature of the carbon mass accumulation evolution (Figure 3). The model does not a priori assume any process to be responsible for the curvature (Pirk et al., 2016). In the case of the measurement of CO₂ flux in soils, the curvature (λ) relates to leakages, diffusivity from soil CO₂ into the chamber headspace and

photosynthesis (Kutzbach et al., 2007). In the case of our chambers drilled in rock, since it is assumed that there is no possibility

of photosynthesis, λ likely relates to the diffusivity of carbon from the rock to the chamber headspace and to the chamber leakiness. Equation Eq. (7) is solved by fitting the following function to the data (Figure 3B):

$$m(t) = \frac{q}{\lambda} \left(1 - \exp(-\lambda t) \right) + m_0 \tag{8}$$

For the sake of comparability and automatization, all curves of carbon mass accumulation were fitted for periods of 6 minutes after the rate of carbon mass change variability over a moving 10 second window was below a certain threshold (1x10⁻⁴ mg.s⁻⁺ for 20 seconds was empirically found suitable; Figure 3B).

Several parameters lead to uncertainties Θ in the flux calculations. They are all related to the conversion of pCO₂ to mass of carbon (Table 1): i) the volume of the chamber ($\forall_{CH}, \forall_{Ch}$); ii) the surface area of exchange with the surrounding rock (S); iii) the volume of the closed-loop system when air flows through the bypass (V_L was determined to be 127.8 ± 0.5 cm³ through an experiment of successive CO₂ dilution in a known volume); and iv) the temperature in the chamber was assumed to range from 0 to 20°C over the course of the experiment. We estimated the relative uncertainty on the measured flux using a Monte-Carlo simulation of error propagation using the ranges listed above and in Table 1. The resulting relative uncertainty on the measured flux was estimated to be within ± 2.5 %. An additional relative uncertainty linked to the rate of CO₂ accumulation in the chamber (parameter q obtained through fitting the exponential model to the data) ranges between 0.5 to 1.0_%. Altogether, the final relative uncertainty determined with our Monte-Carlo simulation of error propagation was found to be within ± 2.73_-%. In the case that the relative standard deviation on multiple flux measurements is higher than 2.73_%, we adopt the standard deviation as the uncertainty.

2.4 CO₂ sampling and isotopic analysis

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CO₂ evading the rock accumulates in the chamber and can be sampled using a zeolite molecular sieve trap (Garnett et al., 2009; Garnett and Hardie, 2009; Hardie et al., 2005). Zeolites have a high affinity for polar molecules such as H₂O and CO₂, and are widely used to separate CO₂ from air at ambient temperature and pressure. The gas trapped by the zeolite sieve can be extracted in the laboratory at high temperature for CO₂ purification and isotope analysis (Garnett and Murray, 2013; Hardie et al., 2005). The type of zeolite (13X) and the design of the cartridge containing the zeolite, is described by Hardie et al. (2005) and Garnett et al. (2009). In our study the CO₂ was sampled 'actively' – i.e., using the CO₂ sampling system coupled to the

- 25 pump incorporated in the IRGA to force the air through the zeolite molecular sieve cartridge (Figure 1) following Hardie et al. (2005). Two approaches can be used. The first involves connection of the line to the chamber for the duration of trapping, which was used on 27/03/2017. Each removal of CO₂ onto the trap can be controlled to return the chamber to ambient atmospheric pCO₂, allowing for a subsequent measurement of CO₂ flux (Figure 3). The second approach allows pCO₂ to accumulate in the chamber, before attaching the scrubbed line and removing the CO₂, which we tested on 30/03/2017. The
- 30 benefit of the latter method is that it allows the gas line and IRGA to be used for other tasks while in the field, but may be more susceptible to atmospheric inputs during the connection of lines.



The CO_2 was also sampled 'passively', when the zeolite molecular sieve is connected to the chamber for several months following the procedure described in Garnett et al. (2009) (Figure 4). This approach has the benefit of providing an integrative view of CO_2 production over longer periods of time. A passive trap was installed on the 15th December 2017 (2 days after the chamber was constructed) and removed on the 26th March 2017 (101 days after its installation) for chamber H6. Based on

- 5 previous work (Garnett et al., 2009; Garnett and Hardie, 2009<u>; Garnett and Hartley, 2010</u>), it is expected that the passive trap method can lead to an isotope fractionation of <u>the stable carbon isotope composition</u> (δ^{13} C<u>) of ~ 3.50 ± 0.45 ‰ 4.2 ± 0.3 ‰</u> associated with the diffusion of CO₂ from the chamber to the zeolite trap. In addition, a sample of local atmospheric CO₂ was also collected –by actively circulating the atmosphere sampled at ~ 3m elevation above the valley floor through a zeolite molecular sieve.
- After sample collection the zeolite molecular sieves were sealed with WeLock® clips on either end before being disconnected from the sampling system (active or passive) and returned to the NERC Radiocarbon Facility (<u>East Kilbride, UK)</u> for CO₂ recovery. The CO₂ collected was desorbed from the zeolite by heating (425°C) and cryogenically purified (Garnett and Murray, 2013). One aliquot of the recovered CO₂ was used for <u>stable carbon isotope composition</u> (δ¹³C) measurement using Isotope Ratio Mass Spectrometry (IRMS; Thermo Fisher Delta V; results expressed relative to the <u>Vienna Pee Dee Belemnite</u> (VPDB)
- 15 standard). A further aliquot was converted to graphite and analysed for ${}^{14}C/{}^{12}C$ ratio using accelerator mass spectrometry at the Scottish Universities Environmental Research Centre (SUERC). –Radiocarbon results-measurements were, following convention, corrected for isotopic fractionation using the measured sample IRMS $\delta^{13}C$ values, and reported in the form of the fraction modern (Fm) [A_{SN}/A_{ON} in Stuiver and Polach (1977); corresponding to ${}^{14}a_N$ in Mook and van der Plicht (1999), or F¹⁴C in Reimer et al. (2004)] (Table 2).

20 2.5 Partitioning the sources of CO₂

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As the chamber was were-drilled away from the obvious influence of root respiration, the CO_2 emanating emitted from the rock should originate from: i) the oxidation of the organic carbon contained within the rock mass following Eq. (1); and/or from ii) the dissolution of the carbonate minerals by sulphuric acid following Eq. (2). Some of the CO_2 collected in active or passive zeolite molecular sieves might also originate from atmospheric CO_2 , i.e., the ambient air (see discussion below). To correct for possible atmospheric contamination, and partition the sources of CO_2 , we solve the following isotope-mass balance system:

$$\begin{cases} f_{Atm} + f_{Rock OC} + f_{Carb} = 1\\ f_{Atm} \cdot \delta^{13} C_{Atm} + f_{Rock OC} \cdot \delta^{13} C_{Rock OC} + f_{Carb} \cdot \delta^{13} C_{Carb} = \delta^{13} C_{Chamber}\\ f_{Atm} \cdot Fm_{Atm} + f_{Rock OC} \cdot Fm_{Rock OC} + f_{Carb} \cdot Fm_{Carb} = Fm_{Chamber} \end{cases}$$

where, f_{Atm} is the mass fraction of CO₂ originating from the atmosphere, $f_{Rock OC}$ is that originating from the oxidation of the rock-derived organic carbon and, f_{Carb} is that originating from carbonate dissolution by sulphuric acid. Subscript "Chamber" stands for <u>the CO₂</u> sampled from the chambers and extracted from the zeolite molecular sieves(i.e., trapped in the zeolite

(9)

molecular sieves). δ^{13} C and Fm stand for the stable carbon isotope and radiocarbon compositions of the three possible sources of CO₂ listed above and of the CO₂ sampled in the chamber.

Table 3 shows the δ¹³C and Fm values of the three possible sources of CO₂ involved in the isotope-mass balance. These values were measured in the laboratory. The δ¹³C_{Atm} and Fm_{Atm} values were measured from the atmospheric CO₂ sample actively trapped in a zeolite molecular sieve (see Sect. 2.4.). The δ¹⁴C-stable carbon isotope composition-(vs. VPDB) of the rock-derived organic carbon <u>(δ¹³C_{Rock OC})</u> was obtained by IRMS after inorganic carbon removal from the rock powdered samples by HCl fumingation, followed by closed-tube combustion to produce CO₂. The δ¹⁴C-stable carbon isotope composition of the carbonates <u>(δ¹³C_{Carb})</u> was obtained after dissolution of the carbonates of the rock powdered samples by phosphoric acid in vacuumed vessels following standard procedures at NERC Radiocarbon Facility-(East Kilbride, UK). Since the rock-derived
organic carbon and carbonates were formed millions of years ago they should do not contain radiocarbon any longer, and their

<u>fraction modern ($Fm_{Rock OC}$ and Fm_{Carb})</u> levels should be close to the AMS background <u>as confirmed by our measurements</u> (Table 3). <u>Consequently, when solving the isotope-mass balance, $Fm_{Rock OC}$ and Fm_{Carb} were set to 0.</u>

3 Results and Discussion

Here we present the results (<u>Table 2, 3, 4 and Figures 2 and 3</u>) obtained from a natural weathering chamber (H6) drilled <u>in a</u>
<u>rock face at 2 meters elevation above the Laval stream (Figure 1</u>) in December 2016. Our aim is to assess the feasibility of the method, in terms of: i) measuring the fluxes of CO₂; ii) collecting sufficient mass of CO₂ for isotope analysis (to partition between organic and inorganic derived CO₂); and iii) checking the role of atmospheric CO₂ contamination for both the active and passive CO₂ sampling methods. We discuss the results from chamber H6 in the context of using this method more widely to better quantify rates of oxidative weathering and associated CO₂ release.

20 3.1 Flux Measurementsmeasurements

Three months after the installation of the chamber H6, CO₂ fluxes were measured alongside a series of zeolite-trapping events on 27/03/2017 (Figure 3). If the chamber was perfectly isolated from the atmosphere, then we might expect the rate of carbon accumulation $\left(\frac{dm(t)}{dt}\right)$ to be constant, while it decreases with time. As expected, this indicates that the chamber is not perfectly sealed. This has some important implications. First, the leak rate depends on the pCO₂ gradient between the chamber and the atmosphere. Since this gradient is positive in the chamber (Figure 2) $(pCO_{2chamber} > pCO_{2atmosphere})$, then CO₂ likely diffuses from the chamber to the atmosphere. This has the advantage that it naturally minimizes any atmospheric CO₂ contamination. Conversely, since the CO₂ production is linked to the consumption of O₂, then the O₂ gradient is expected to be negative $(pO_{2chamber} < pO_{2atmosphere})$, and thus atmospheric O₂ naturally diffuses inside the chamber. This means that the chamber can be closed for months and still contain gaseous O₂. Our measurements of O₂ using the EGM-5 O₂ probe suggest

that the chamber had a similar pO_2 as that contained in the ambient atmosphere of the catchment (the chamber value was 96 to 99% of the atmosphere pO_2).

The fluxes of CO₂ measured in this chamber on 27/03/2017 decreased from $529 \pm 14 \text{ gC.m}^2 \cdot \text{yr}^4 - \underline{1384 \pm 42 \text{ mgC.m}^2 \cdot \text{day}^{-1}}$ to $\underline{266 \pm 7 \text{ gC.m}^2 \cdot \text{yr}^4} \cdot \underline{684 \pm 21 \text{ mgC.m}^2 \cdot \text{day}^{-1}}$ with the number of times we extracted the CO₂ from the chamber (Figure 3).

- 5 The flux becomes approximately constant after three CO₂ extractions during zeolite trapping, with an average of 272±8 gC.m⁻
 ²·yr⁺ 705 ± 15 mgC.m⁻².day⁻¹ (1sd, n=4) for the last 4 flux repeatsmeasurements that are iundistinguishable from each other within 2σ (Figure 3). This observation might be explained by the fact that over time (days to months), CO₂ accumulates not only in the chamber, but also in the regolith/rock connected pores surrounding the chamber in the lower compact regolith (Maquaire et al., 2002)surrounding the chamber. Weathering reactions are likely to occur not only at the chamber-rock interface, but also into the rock mass over several centimetres as the weathered regolith extends to depths of up to 20 cm
- (Maquaire et al., 2002; Mathys and Klotz, 2008; Oostwoud Wijdenes and Ergenzinger, 1998). When CO₂ is first extracted from the chamber, the CO₂ stored in the surrounding pores quickly refills the chamber. It appears that after three extractions this CO₂ is depleted, meaning that the more constant values correspond to the actual flux of CO₂
- through the surface area of the chamber. We would therefore recommend that flux measurements are made on such a chamber
 following ~3 to 4 removals of CO₂, or adapted to less or more removals based on the results obtained after a series of flux measurements. It remains to be seen the degree to which this feature is widespread, or chamber specific.
- It has to be noted that the mass of carbon (m_C) recovered on the zeolite molecular sieve during the period of passive trapping (Δt) cannot be directly and simply used to inform the flux of carbon through the chamber. This is because the rate of carbon trapping (m_C/Δt) follows the first Fick's law (Bertoni et al., 2004) and hence depends on the partial pressure of CO₂ in the
 chamber rather than on the flux itself. It is thus not trivial to assess the flux from the rate of carbon passive trapping (m_C/Δt)
- as the flux itself may change through time. Similar reasons prevented the direct use of the amount of passively trapped CO₂ to estimate flux rates in previous studies (Hartley et al., 2013). Nevertheless, the rate at which CO₂ is trapped on the zeolite molecular sieve ($m_C/\Delta t$) is still qualitatively informative about CO₂ flux when compared to other sampling periods when CO₂ is passively trapped (see the Appendix for further information).
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3.2 Isotope measurements and isotopic fractionation

3.2.1 Active sampling method

The atmospheric CO₂ was sampled on 27/03/2017, yielding a δ¹³C of -9.6‰ and a ¹⁴C activity of Fm=1.0065±0.0044. From chamber H6, we sampled CO₂ twice actively on 27/03/2017 (by in line trapping, Figure 3) and on 29/03/2017 (by repeated trapping over the course of a day) both yielding ~2.1 mgC. The ¹⁴C activities (Fm of 0.0597±0.0047 and 0.0562±0.0047, respectively) were identical within measurement uncertainty. Because the CO₂ originating from rock-derived organic matter and carbonate minerals is ⁽¹⁴C-dead', as confirmed by ¹⁴C measurements of the organic carbon and carbonate of the rock from

the studied chamber (Table 3), the atmospheric CO₂ input (f_{Atm}) can be calculated as $f_{Atm} = Fm_{Chamber}/Fm_{Atm}$. The Fm from both samples shows that only ~5.5% to 6% of the CO₂ trapped was of atmospheric origin and that the two active trapping methods produce comparable results. The δ^{13} C compositions (-7.4‰ and -6.1‰, respectively) were within the range expected for a mixture of organic and inorganic carbon derived CO_2 , but differed by ~1 ‰ for these two traps (Table 2).

- 5 It has been shown that actively trapping of CO₂ from headspace chambers does not induce any δ^{13} C fractionation because of near complete recovery of the CO₂ present in the chamber (Hardie et al., 2005). Thus the difference in the δ^{13} C composition between our two actively trapped CO₂ samples may reflect different relative rates of carbonate dissolution by sulfuric acid versus organic matter oxidation over a daily timescale, which is an observation worth exploring in more detail. Such changes in the δ^{13} C composition of the CO₂ sampled from field-based chambers on soils or streams have already been observed and
- 10 may stem from natural environmental changes over the course of the experiments (Garnett and Hartley, 2010; Garnett et al., 2016). We cannot exclude that some diffusive processes (Davidson, 1995) within the rocks surrounding the drilled chambers or some leakage around the chamber entrance may have induced the observed 1% difference between our two actively trapped CO2 samples. However, these samples were collected from the exact same chamber that is likely characterized by the same diffusive processes and leakage over days. If so, the observed 1‰ is likely due to natural environmental changes in the CO2
- 15 production rather than due to diffusive processes or major leaks.

3.2.2 Passive sampling method

From chamber H6, the CO₂ sample passively trapped for 101 days from mid-December 2016 to late March 2017 yielded ~11.4 mgC. The sieve cartridges have been shown to reliably trap >100 ml CO₂ (Garnett et al., 2009; i.e. > ~50 mgC), so the 11.4 mgC from H6 represents less than a quarter of the sieve capacity, suggesting that passive sieves can be left for at least ~6 months without becoming saturated with CO2 at this field site (in reality, saturation by water vapour may be more likely to be

- a limiting factor). The Fm was 0.0495±0.0047, which is very similar to the active trapping results, with only ~5% atmospheric CO2 contamination. This is perhaps surprising since the trap was left exposed in the natural environment for three months. However, it results from the high pCO₂ present in the chamber throughout the time period, driving a net diffusive transfer of CO2 from chamber to the zeolite sieve. It suggests the components used to make the chamber and its linkages are not susceptible
- 25 to major leaks.

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The δ^{13} C composition of the passively trapped CO₂ was -9.4‰ and has to be corrected for a fractionation factor of 4.2 ± 0.3 ‰ associated with the passive trapping method (Garnett and Hardie, 2009; Garnett and Hartley, 2010) to provide the actual average δ^{13} C composition of the CO₂ during the duration of the experiment (here ~3 months). This fractionation is due to the diffusive transport of CO₂ through air from the chamber to the zeolite molecular sieve (Davidson, 1995). The δ^{13} C composition

30 of the passively trapped CO₂ sample, displaysing a 2.0% and 3.3% depletion when compared to the δ^{13} C values obtained with the actively trapped CO2 samples trapping method. This suggests that fractionation during passive trapping actually occurred, in agreement with earlier studies (Garnett et al., 2009; Garnett and Hardie, 2009; Garnett and Hartley, 2010). Garnett et al. (2009) and Garnett and Hardie (2009) who show a 3.50 ± 0.45‰ fractionation associated with the passive trapping method.

The fractionation is likely due to the diffusion of CO₂ through air (Davidson, 1995). However, the δ^{13} C difference between actively and passively trapped CO₂ samples is less than the expected 4.2‰ value. It has to be noted that the passive sampling method averages ~3 months of CO₂ δ^{13} C composition in the chamber, while the active sampling method averages only a few hours. Thus, the apparent "mismatch" may be due to naturally changing CO₂ δ^{13} C composition over time scales shorter than

5 ~3 months and likely of the order of hours to days. This shows that both active and passive methods are complementary methods making us able to explore different timescales of sedimentary rock weathering.

3.2.3 The source of the CO2: rock-derived organic carbon oxidation vs. carbonate dissolution by sulphuric acid

We solved the isotope-mass balance Eq. (9) for the actively trapped CO₂ samples from 27/03/2017 and 30/03/2017, and for the passively trapped CO₂ sample (Table 4). The δ¹³C of the passively trapped CO₂ was corrected using the published 3.50 ± 0.454.2 ± 0.3 ‰ fractionation factor (Garnett et al., 2009; Garnett and Hardie, 2009; Garnett and hartley, 2010) prior to calculations, and the ¹⁴C activity of both the rock-derived organic carbon and carbonate end-member were set to 0, as their measured Fm were close to instrumental background (Table 3). We found very similar results for the three trapped CO₂ samples, yielding 5% to 6% of CO₂ from atmospheric contamination, 71% to 7779% of CO₂ from the dissolution of the carbonates by sulphuric acid and 1916% to 23% of CO₂ from the oxidation of rock-derived organic matter (details in Table 4).

15 The proportion of the CO_2 derived from the oxidation of rock organic carbon ($f_{Rock OC}$) and that derived from the dissolution of carbonate by sulfuric acid (f_{Carb}) are A correction corrected for the ingress-contamination of atmospheric CO_2 is applied tobefore the partitioning of the measured CO_2 flux-of CO_2 . Corrected proportions (f_x^* , where subscript "x" is "Rock OC", or "Carb") are calculated based on the proportions (f_x) found after solving the isotope-mass balance as follows:

$$f_{x}^{*} = f_{x}/(1 - f_{Atm})_{-}$$

(10)

- This shows <u>1917</u>% to 24% from rock-derived organic carbon and 76% to <u>8183</u>% from carbonate dissolution (Table 4). Therefore, for chamber H6 on 27/03/2017 for which we simultaneously measured the bulk CO₂ flux (<u>272 ± 8 gC.m⁻².yr⁻¹</u>)<u>705</u> <u>± 21 mgC.m⁻².day⁻¹</u>), these proportions equate to a flux of <u>171 ± 5 mgC.m⁻².day⁻¹ 66 ± 2 gC.m⁻².yr⁻¹</u>-derived from the natural oxidation of rock organic matter, and a flux of <u>534 ± 16 mgC.m⁻².day⁻¹ 206 ± 6 gC.m⁻².yr⁻¹</u>-derived from the dissolution of carbonates by sulphuric acid (Table 4).
- At the scale of chamber H6, these flux measurements imply that over a year <u>~116109</u> grams of rock would be weathered by sulphuric acid to produce the carbonate-derived CO₂ flux (i.e., <u>7.67.1</u> gC produced in one year from a rock with 6.52 w% of inorganic carbon). In contrast, <u>~22102080</u> grams of sedimentary rock would need to have been oxidized to produce the rock-organic carbon CO₂ flux (i.e., <u>2.42.3 gC</u> produced in one year from a rock with 0.11 w% of organic carbon). The dissolution of carbonate depends on the oxidation of sulphides, and may therefore only occur locally where sulphides are concentrated.
- 30 <u>Based on these first measurements from one chamber</u>, <u>The oxidation of organic carbon appears to occur more homogeneously</u> in the rock mass.

3.3 First order comparison of the magnitude of our CO₂ fluxes with other methods estimating CO₂ fluxesNatural flux of CO₂ evading sedimentary rocks

To our knowledge, we report here the first attempt to directly measure directly the CO_2 flux emitted during weathering of sedimentary rocks, and trap this CO_2 to partition its sources using stable carbon isotopes and radiocarbon-composition. We

- 5 acknowledge that our field-based experimentschamber method has have not been replicated, representing a limitation to our study. Nevertheless, our study is a field-based experiment, where many environmental parameters (e.g., temperature, precipitation, water content in the unsaturated zone...) will have an impact on the weathering and erosion of the studied marks. Hence we expect that the CO₂ flux we measured in March 2017 and its isotopic composition will be different from measurements carried out at another times during the following monthsof the year. Similarly, due to the marl geochemical
- 10 heterogeneities (e.g., inorganic and organic carbon contents, as well as content in sulphide mineral), the CO₂ flux and its isotopes could be expected to vary from a-one chamber to another. It is thus impossible to replicate the exact same results we present here. We propose that future work should aim to monitor numerous chambers over seasonal changes in environmental conditions.
- While wary of these caveats, Jin the following sections we compare our results with other methods, to test the order of magnitudes of the CO₂ flux we obtained using our cylindrical chambers against previously published estimates from other regions of the world. While this exercise is challenging due to major differences in the way the CO₂ fluxes were estimated and in the surface area and time scales (local estimates at a fixed time vs. regional estimates averaged over months/years), it is informative to assess the reliability of our method.

3.3.1 Rock-derived organic carbon oxidation

- 20 The flux of CO₂ originating from the oxidation of rock-derived organic carbon is difficult to assess. To our knowledge, there has only been one direct estimate of 0.5 gC.m⁻².yr⁻¹ using modelling of vadose CO₂ and its isotopes in Saskatchewan (Canada) (Keller and Bacon, 1998). This is <u>130-120</u> times lower than our estimate in the chamber H6 of the Laval catchment (i.e., <u>171</u> ± 5 mgC.m⁻².day⁻¹ scaled to a year, giving 62 ± 2 gC.m⁻².yr⁻¹). This might be explained by the much lower erosion rates of the Canadian site, with deep soils and stable geomorphology, compared to the Laval catchment where erosion continuously
 25 exposes rocks to oxidative weathering (Graz et al., 2012).
- CO_2 fluxes derived from the oxidation <u>of</u> rock organic carbon have been indirectly estimated using geochemical proxies, such as dissolved rhenium fluxes in rivers (Dalai et al., 2002; Hilton et al., 2014; Horan et al., 2017). Our direct measurements obtained from a single chamber (H6) (<u>66–62</u> ± 2 gC.m⁻².yr⁻¹) are of the same order of magnitude as that calculated in highly erosive Taiwanese catchments <u>using dissolved rhenium yields and the loss of rock organic carbon from soils</u> (5 to 35 gC.m⁻²
- 30 ².yr¹) (Hilton et al., 2014<u>; Hemingway et al., 2018</u>). It is clearly too early to directly relate these fluxes. It is likely that individual chambers have different CO₂ fluxes (possibly depending on rock-heterogeneities in the rock physical and geochemical properties heterogeneity, temperature, water supply to the unsaturated zone), and that CO₂ fluxes from a single chamber may vary throughout the year. Nevertheless, our proof of concept study suggests that direct measurements are

consistent with proxy-based methods. The spatial variability in oxidation rates and its variability throughout the year are important questions which can be tested with the chamber method we describe here.

3.3.2 Carbonate dissolution by sulphuric acid

Inorganic carbon was the main source of the CO₂ flux measured during our experiment (i.e., 534 ± 16 mgC.m⁻².day⁻¹ scaled to
<u>a year, giving 206-195</u> ± 6 gC.m⁻².yr⁻¹). The dissolution of carbonate minerals by sulphuric acid (i.e., by oxidized sulphide minerals) is the simplest explanation (Calmels et al., 2007). An implication of this result is that in the Laval catchment, carbonates are weathered preferentially according to Eq. (2), i.e., immediately-releasing CO₂ to the atmosphere at the weathering site. This statement is supported A study reportingby the average anion concentrations in the Laval stream in 2002 (Cras et al., 2007) that gives a low bicarbonate-to-sulphate ratio (HCO₃⁻/SO₄²⁻ -0.35). ratio of ~0.35). At first order (i.e., assuming that sulphate is exclusively derived from oxidized sulphides), this observation supports the fact that carbonate weathering preferentially produces gaseous CO₂ (Eq. (2), i.e., HCO₃⁻/SO₄²⁻ HCO₃⁻/SO₄²⁻ = 0) ratio equal to 0) instead of dissolved inorganic carbon (Eq. (3), i.e, HCO₃⁻/SO₄²⁻ HCO₃⁻/SO₄⁻ HCO₃/SO₄⁻ HCO₃⁻/SO₄⁻ H

- 15 The published river ion data can be used to estimate the weathering of carbonate minerals by sulphuric acid. From the average Ca²⁺ and SO₄²⁻ concentrations measured in 2002 and the average runoff (Cras et al., 2007), assuming that the weathering of carbonates produced only gaseous CO₂, we estimate a flux of CO₂ to the atmosphere of 19 to 37 gC.m⁻².yr⁻¹. These values could be refined by measurement of sulphur and oxygen isotopes of SO₄²⁻ to partition sulphate source (Calmels et al., 2007). Although of the same order of magnitude, tThe river ion flux estimate is much lower than our direct measurement. This is likely due to the fact that we compare here an isolated (metre-scale) measurement to a catchment-scale average estimate which
- takes into account regions that have lower erosion and weathering rates. A complementary explanation would be that the flux of CO₂ emitted during weathering may change seasonally as a response to changes in temperature and water content in the unsaturated zone. Thus the flux we measured directly would be lower if averaged over the course of a year, hence including winter months with expected lower fluxes. This necessitates monitoring over months.
- Our local direct measurement is higher than the <u>annual flux estimate</u> obtained for a similar highly erosive catchment in Taiwan (Liwu River) using dissolved river chemistry <u>ofand showing a value of</u>_~20 gC.m⁻².yr⁻¹ (Calmels et al., 2011; Das et al., 2012; Torres et al., 2014). These values are much higher than that of less erosive major river systems like the Mackenzie River in Canada (Calmels et al., 2007; Torres et al., 2014) (<1 gC.m⁻².yr⁻¹) or the Ganges-Brahmaputra river system in India (<1 gC.m⁻².yr⁻¹) (Galy and France-Lanord, 1999; Torres et al., 2014), and supports <u>an important the strong</u> control of physical erosion in the weathering of carbonates via oxidative weathering of sulphides. Our chamber-based method provides a new way

to quantify this process in the field, and assess the spatial and temporal variability in CO₂ production by this weathering process.

4 Conclusions

Here, we present a reliable, innovative and relatively inexpensive way to measure the flux of CO₂ produced during the oxidative
weathering of sedimentary rocks. The ability to trap the CO₂ using active or passive zeolite molecular sieves is essential, since its carbon isotopic composition (¹²C, ¹³C, ¹⁴C) is mandatory to assess for atmospheric CO₂ inputs, before partitioning the CO₂ flux between that from oxidation of rock-derived organic carbon and carbonate dissolution by sulphuric acid. The passive method to trap the CO₂, i.e., leaving zeolite molecular sieve connected to a chamber for days to months, is useful to provide a time integrative sample of CO₂ produced during weathering. This paper is a proof of concept of the oxidative weathering of rocks: i) rock-derived organic carbon is oxidized and CO₂ is released directly to the atmosphere and its flux can be large enough to be directly measurable; ii) the oxidation of sulphides contained in the rocks produces sulphuric acid and dissolves carbonates <u>and in</u>. In the Laval catchment this phenomenon releases CO₂ directly to the atmosphere-rather than dissolved

Data availability

inorganic carbon, and its flux can be locally large.

15 Raw data and flux resulting from exponential fitting of data are available in the supplementary material.

in the zeolite trap. In this case, first Fick's law may be written as follows:

Appendix

Here we explain how This appendix is meant to show how the mass of CO₂ accumulated on the passive traps over several months- may to be compared to qualitatively relate the amount of carbon passively trapped over long term periods to short-term flux measurements made during the active trapping method. Passive sampling is a practical application of the first Fick's
first law (Bertoni et al., 2004). In our case it is related to the diffusion (D) of CO₂ molecules in air caused by the gradient of CO₂ partial pressure between that of the chamber (pCO_{2,4Cb}) and that of the zeolite trap (pCO_{2,2colite}). This diffusion is defined for a length of time (Δt) and is limited to the internal side of the tube linking the chamber to the zeolite trap, i.e. the diffusion path characterized by the tube length (L) and tube section area (a). It results in the trapping of a certain mass of carbon (m_C)

25
$$pCO_{2,Ch} - pCO_{2,zeolite} = \frac{m_C}{\Delta t} \frac{RT}{pM_c} 10^6$$
 (A-1)

R is the gas constant, T is temperature, P is pressure and M_C is the molar mass of carbon. Factor $10^6 \times RT/PM_C$ converts grams of carbon to cm³ of CO₂, and pCO₂ is here in ppm (cm³/m³). Note that the pCO_{2,zeolite} in the zeolite trap is equal to 0 ppm, since the zeolite is the CO₂ absorber. The equation thus reduces to:

$$pCO_{2,Ch} = \frac{m_C}{\Delta t} \frac{L}{aD} \frac{RT}{PM_C} 10^6$$
(A-2)

5 Equation (A-2) can be used reconstruct the average partial pressure of CO_2 in the chamber $pCO_{2,Ch}$ during the sampling duration (Δt). Eq. A-2 also indicates that the passive trapping is only directly linked to the partial pressure in the chamber over the sampling length of time Δt . In other words, passive sampling is not related in a simple way to the flux of CO_2 through the chamber.

In order to relate long-term passive sampling to short-term CO₂ flux measurements, we assume that the evolution of the pCO₂ in the chamber can be described following an exponential law (Pirk et al., 2016; see Eq. 7-8 of main text), and we can describe the pCO_{2xCb} in the chamber based on other parameters:

$$pCO_{2,Ch} = \frac{1}{V_{Ch}} \left[\frac{q}{\lambda} \left(1 - \exp(-\lambda \Delta t) \right) + m_0 \right] \frac{RT}{PM_C} 10^6$$
(A-3)

 V_{Cb} is the volume of the chamber, q is the initial rate of carbon accumulation in the chamber, m_0 is the initial mass of carbon in the chamber (a value that corresponds to 400ppm of CO₂ in the volume of the chamber). λ , per unit of time, is the parameter

15 that describes the diffusive processes responsible for the non-linear accumulation of carbon in the chamber. In the case of longterm passive sampling Δt is very large (~3 months and thus ~150,000 minutes). Thus exp($-\lambda\Delta t$) tends to 0 and Eq. A-3 simplifies to:

$$pCO_{2,Ch} = \frac{1}{V_{Ch}} \left[\frac{q}{\lambda} + m_0 \right] \frac{RT}{PM_C} 10^6$$
(A-4)

Note that Eq. A-4 can be written only if we assume that the initial rate of carbon accumulating in the chamber (q) does not
 change over time. This is a very large assumption may be that we expect to be violated because q is unlikely to stay constant over time for various reasons including natural variability in CO₂ production and also changes in the diffusive processes (parameter λ) when pCO₂ builds up in the chamber. Equating Eq. A-2 and Eq. A-4, we obtain:

$$\frac{m_{C}}{\Delta t} \frac{L}{aD} \frac{RT}{PM_{C}} 10^{6} = \frac{1}{V_{Ch}} \left[\frac{q}{\lambda} + m_{0} \right] \frac{RT}{PM_{C}} 10^{6}$$
(A-5)

Hence we can derive the rate at which carbon accumulates into the chamber based on the passive trapping parameters and λ_s

25 which is measured in the field over short time periods (i.e., during the short-term flux measurements when CO₂ is actively actively trapped – see Eq. 7-8 in the main text):

$$q = \lambda \left(\frac{m_c L}{\Delta t a D} V_{Ch} - m_0 \right)$$
(A-6)

The flux can be inferred from the later equation using the internal surface area of the chamber (S). If q was in mgC/min, then the flux of carbon Q in mgC/m²/day is:

5
$$Q = \lambda \left(\frac{m_c}{\Delta t} \frac{L}{aD} V_{ch} - m_0\right) 1440/S$$
(A-7)

We can determine most of the parameters of Eq. A-6 independently from the short-term flux (Q or q) measurements, except for λ . For instance m_C, m₀, V_{Ch}, S, Δt , a and L can be measured and D (diffusion of CO₂ in air) can be inferred from the literature. However, λ is determined using the short-term flux measurements, along with the flux (i.e., Q or q). Thus estimating the flux of CO₂ based on the rate of carbon passively trapped in the zeolite trap (m_C/ Δt) is not independent from the short-term

10 CO₂ flux measurements. Hence, comparing a CO₂ flux inferred from the mass of carbon m_C recovered using the passive trap and calculated using Eq. A-6 and Eq. A-7, and the CO₂ flux actually measured during our short-term experiments, is somewhat circular because they are not determined independently from each other.

For longer monitoring of field work sites, the mass of carbon trapped is still qualitatively informative. but only qualitatively since This is because m_{C₇} or better else, and the rate carbon trapping per unit of time (m_C/Δt) are proportional to the flux of carbon Q to the chamber and parameter λ. This is illustrated easily by writing equation Eq. A-7 differently:

$$m_{C/\Delta t} \propto Q/_{\lambda}$$
 (A-8)

where the left-hand part of Eq. 8 are the parameters measured during passive trapping and the right-hand part of Eq. A-8 are the parameters measured during short-term flux measurements. Interpretations of changes in $m_c/\Delta t$ are-thus give qualitative constraint on CO₂ fluxes over time. Future work might investigate whether the parameter λ can be characterised for a chamber

20 independently from the active CO₂ flux measurements. If it can, the passive trap method can be used not only qualitatively (e.g. to look for changes in the mass of CO₂ collected on passive traps through time), but quantitatively (i.e. the monthly timeintegrated CO₂ flux).

Author contribution

RGH conceived the research and designed the study with GS and MHG. GS, RGH and SK carried out chamber installation.
25 GS carried out flux measurements and sample collection with on-field assistance of RGH, MD and MO. GS, RGH, MHG and TC analysed the data. GS, RGH and MHG interpreted the data. GS wrote the manuscript with inputs from RGH and MHG. All co-authors commented on the manuscript.

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Tables

Table 1. Dimensions of a typical chamber^{a, b}

Inner diameter	Depth	PVC tubing	Depth of insertion of PVC tubing	Depth of insertion of rubber stopper	Chamber volume	Area of exchange with surrounding rock
cm	cm	cm	cm	cm	cm ³	cm^2
2.9 (2.8 - 3.0)	41 (40.5 - 41.5)	4 (3.5 - 4.5)	1.5 (1 - 2)	1 (0.75 - 1.25)	281 (252 - 312)	366 (345 - 389)

^aChamber H6 drilled on 13/12/2016 in the catchment of the Laval stream (Draix, France; N44.14061°, E06.36289°)

^bGiven as ranges: median (min - max)

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Table 2. Isotopic composition of the CO_2 sampled with the zeolite molecular sieves

Sample label	Publication number	Method	Mass of carbon sampled (mg)	$\delta^{13}C$ (‰VPDB)	Fraction modern
DRA16-H6-1512-P	SUERC-73091	Passive ^a	11.4	-9.4	0.0495 ± 0.0047
DRA17-H6-2803-A	SUERC-73096	Active	2.1	-7.4	0.0597 ± 0.0047
DRA17-H6-3003-A	SUERC-73094	Active	2.1	-6.1	0.0562 ± 0.0047
DRA17-ATM-2703	SUERC-73095	Active	3.8	-9.6	1.0065 ± 0.0044

^a sampled passively for 100.84 days

Table 3. Geochemical compositions of the end-members involved in the isotopic mass	
balance (Eq. 9) were measured from the rock sampled during the drilling of chamber H6	1
and from an atmospheric CO ₂ sampled actively with a zeolite molecular sieve (Table 2).	

	Content (weight %)	Publication number	$\delta^{13}C$ (‰VPDB)	Fraction modern
Total Inorganic Carbon	6.52±0.6 (n=3)	SUERC-74506	0.3 ± 0.1	0.0032 ± 0.0006
Total Organic Carbon	0.11±0.7 (n=3)	UCIAMS-192874	$\textbf{-30.8} \pm 0.1$	0.0125 ± 0.0039
Atmospheric CO ₂	<u>n/a</u>	SUERC-73095	-9.6 ± 0.1	$\underline{1.0065\pm0.0044}$

^ain house label of this sample was DRA16-78

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Table 4. Isotope-mass balance results

	Sample label	Publication number	Method	Sources	Proportion (%)	Proportion corrected for atmospheric contribution (%)	Partitioned flux (mgC.m ⁻² . yrday ⁻ ¹)
			IERC- Passive ^a	Atmosphere	4.9 ± 0.5	-	-
	DRA16-H6- SUE 1512-P 730	SUERC-		Carbonates	76.7<u>79.0</u> ± 1.<u>51</u>	80.7<u>83.0</u> ± 1. <u>61</u>	-
		75071		Rock Organic Carbon	18.4<u>16.1</u> ± 1.<u>50</u>	19.3<u>17.0</u> ± 1. 61	-
	DRA17-H6- SUERC- 2803-A 73096		Active	Atmosphere	5.9 ± 0.5	_	-
		SUERC- 73096		Carbonates	71.2 ± 0.5	75.7 ± 0.4	$\frac{206 \pm 6534 \pm}{16^{b}}$
			Rock Organic Carbon	22.9 ± 0.4	24.3 ± 0.4	$66-171 \pm 2^{b}5^{b}$	
	DRA17-H6- SUERC- 3003-A 73094		Active	Atmosphere	5.6 ± 0.5	-	-
		SUERC-		Carbonates	75.6 ± 0.5	80.1 ± 0.4	-
			Rock Organic Carbon	18.8 ± 0.4	19.9 ± 0.4	-	

^a before solving isotope-mass balance, the δ^{13} C of the passive sample was corrected for a fractionation factor of 3.50 ± 0.45<u>4.2 ± 0.3 ‰</u> (Garnett et al.and Hardie, 2009; Garnett and Hartley, 2010)

 b from a measured bulk CO_2 flux of $\underline{\text{272-}\underline{705}}\pm\underline{\text{8-}\underline{21}}\,\underline{\text{mgC.m}}^{\text{-2}}.\underline{\text{yrday}}^{\text{-1}}$

Figures



Figure 1: A: Schematic diagram of the closed-loop monitoring-sampling system connected to the natural weathering chamber. Gas flow pathways are controlled by opening and closing the clips. Clips removed from the bypass allow pCO2 in the chamber to be 5 monitored (IRGA stands for Infra-Red Gas Analyzer), thus measuring CO2 flux and ensuring that enough CO2 accumulated in the chamber for ¹⁴C analysis. To remove CO₂ from the line before connecting to the chamber, clips are moved from the CO₂ scrub (soda lime). When connected to the chamber, the CO2 scrub can be used to lower the CO2 concentration before flux measurement. To collect CO₂ in the chamber for isotope analyses, clips are removed from the zeolite molecular sieve cartridge. B: Pictures showing the chamber design. Top picture is chamber (H6), diameter 2.9cm, drilled in the rock on a cleared surface, with white PVC tub ing 10 inserted at the outlet. Bottom picture shows the rubber stopper fitted in the PVC tubing. Two glass tubes go through the rubber stopper and are fitted with Tygon tubing, sealed with the red clips, and the exterior of the chamber is sealed with outdoor sealant. C: View of the field site showing two chambers (top chamber is H6 and lower chamber is H4). The lower chamber is connected to the closed-loop system and is being monitored for flux measurement. The two large grey PVC tubes attached to the rock on the right of the chambers are cases in which zeolite molecular sieves are installed and left for months when connected to the chamber for 15 passive CO₂ trapping.



Figure 2: An example of the monitoring of the CO₂ accumulating in a chamber. The orange curve is the partial pressure of CO₂ (pCO₂, in parts per million volume) through time in chamber H6 on 27/03/2017. A: The CO₂ sampling-monitoring system is not connected to the chamber. Atmospheric CO₂ has been removed from the system (pCO₂ = 0 ppm) using the CO₂ scrub cartridge. B:
The closed-loop monitoring system has been connected to the chamber. pCO₂ increases to reach a maximum value of ~5100 ppm, then drops and equilibrates to ~3500ppm. This pattern reflects the increase in the total volume (by the volume of the CO₂ sampling-monitoring system) which decreases pCO₂ and requires some time for the pCO₂ to equilibrate. We determined that when connected to the chamber, the maximum value of pCO₂ read is 0.94 the actual pCO₂ in the chamber. C: The CO₂ in the chamber is lowered (scrubbed with the CO₂ scrub, or trapped with the zeolite molecular size) to near atmospheric pCO₂. D: residual CO₂ that in the 10 chamber how of CO₂ from the rock surface to the chamber.









Figure 3: A: Series of carbon flux measurements for chamber H6 on 27/03/2017. CO₂ concentration (pCO₂) was converted into mass of carbon (mgC) following Eq. (4) and Eq. (5). Flux of CO₂ – the numbers associated to shaded boxes – are given in mgC.m⁻².yrday⁻¹. B: Close–up of how fluxes were calculated from the rate of carbon accumulation (parameter q) by fitting the exponential model described in Eq. (7) and (8) for 6 minutes (shaded box) after a 10-see moving window variability in the rate of mass carbon change (blue curve) was below a threshold of 10^{-4} mgC.min⁺¹ (red line).



Figure 44: A: Zeolite molecular sieve connected to a chamber for passive CO_2 trapping. The zeolite molecular sieve is encased in the grey PVC tubing and connected for months to the chamber using a white connector. B: Zeolite molecular sieve ready to be disconnected from chamber. The red clips are positioned so that they seal both the zeolite molecular sieve and the chamber.