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Technical note: *in situ* measurement of flux and isotopic composition of CO_2 released during oxidative weathering of sedimentary rocks

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Abstract. Oxidative weathering of sedimentary rocks can release carbon dioxide (CO_2) to the atmosphere and is an important natural CO_2 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 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 measure CO_2 production during the oxidative weathering of shale bedrock, which can be applied in erosive environments where rocks are exposed frequently to the atmosphere. The chamber is drilled directly into the rock face and is a relatively low cost method to provide a long-lived (several months or more), oxygenated environment in contact with a surface area of potential reactant. To partition the measured CO_2 fluxes and the source of CO_2, we use zeolite molecular sieves to trap CO_2 'actively' (over several hours) or 'passively' (over a period of months). The approaches produce comparable results, with the trapped CO_2 having a fraction modern ranging from 0.05 to 0.06 and demonstrating relatively little contamination from local atmospheric CO_2 (fraction modern of 1.01). We use stable isotopes of the trapped CO_2 to partition between an organic and inorganic carbon source. The measured fluxes of rock-derived organic matter oxidation and carbonate dissolution by sulphuric acid from a single chamber were high, but consistent with the high erosion rate of the study region (of ~5 mm yr^{-1}). We propose our in situ method has the potential to be more widely deployed to directly measure CO_2 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 ~1.25×10^7 PgC contained within organic matter and ~6.53×10^7 PgC as carbonate minerals (Sundquist and Visser, 2005). If these rocks are exposed to Earth's oxygenated surface, 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 rock-

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derived organic carbon (Berner and Canfield, 1989; Petsch, 2014), which can be expressed by the (geo)respiration of organic matter:

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \quad (1)$$

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:

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

or

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

In the case of Eq. (1) and Eq. (2), CO_2 is released to the atmosphere "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 (~10^4 to 10^6 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 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 CO_2 and O_2, 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 CO_2 sources. These include the use of geochemical proxies in rivers, which indirectly track 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 CO_2 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 (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 SO_4^{2-} has been assessed using sulphur and oxygen isotopes (Calmels et al., 2007) and/or using the dissolved inorganic carbon flux and its $\delta^{13}C$ composition (Galy and France-Lanord, 1999; Li et al., 2008).

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

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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 (^{12}C, ^{13}C and ^{14}C) of the CO_2 (Keller and Bacon, 1998). Only with that information can the measured CO_2 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 CO_2 released during the oxidative weathering of sedimentary rocks; and (2) trap the CO_2 produced during weathering in order to measure its isotope composition, and partition the source of the CO_2 flux between rock-derived organic carbon and carbonate. Here we outline the chamber-based method to measure CO_2 fluxes, and provide the first examples of active and passive methods to trap CO_2 and use its isotope composition to directly quantify the rate of weathering reactions.

2 Method

2.1 Study area

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 km^2) 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 catchment is composed of Callovo-Oxfordian marls, 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 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 density of ~2.2 t m^{-3}, this equates to a physical erosion rate of ~5 mm yr^{-1}. 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 CO_2 accumulation chambers

In order to measure the flux of CO_2 produced by oxidative weathering of sedimentary rocks, and accumulate enough CO_2 to perform carbon isotope 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), CO_2 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 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.

After measuring the dimensions of the chamber, its entrance is fitted with a small PVC tube (~3cm-diameter, ~3cm-long), which allows a tight seal with an inserted rubber stopper containing two holes. Two Pyrex® tubes (ID=3.4mm and OD=5mm; one of 12cm-long and one of 7cm-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 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 introducing an oxygen-rich atmosphere in the chamber. If gaseous O_2 is consumed (e.g. by Eq. (1)), this would create a gradient in the partial pressure of O_2 (pO_2) whereby the atmosphere surrounding the rock and chamber is of higher pO_2. Given the natural porosity and permeability of the shale bedrock, any diffusion of O_2 is likely to be into the chamber. This should act continuously to fuel the chamber with oxygen. In contrast, if CO_2 is produced inside the chamber (by Eq. (1) and Eq. (2)) then the partial pressure of CO_2 (pCO_2) will exceed that of the atmosphere. The result is that for chambers where oxidative weathering is occurring, the ingress of and 'contamination' by atmospheric CO_2 should be minimal, and there should be a supply of O_2 for reactions. These inferences can be tested using a pO_2 probe and by trapping CO_2 and measuring its isotope composition.

In this example we aimed to measure oxidation of sedimentary rocks, and intended to minimise the role of CO_2 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 to fine powder for measurement of its organic-inorganic carbon content and its isotopic composition.

2.3 CO_2 flux measurements

A closed-loop CO_2 sampling system similar to the molecular sieve sampling system (MS^3) described in Hardie et al. (2005) was used for CO_2 flux measurements and CO_2 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 pCO_2 range of 0 to 5000 ppmv and installed with an pO_2 probe (EGM-5, PP Systems, UK), a CO_2 scrub (cartridge filled with soda lime), a bypass, and a set of WeLock® clips that allows the air flow to be diverted

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through the bypass or the CO_2 scrubber cartridge. Optionally a zeolite molecular sieve sampling cartridge can be inserted in the line (see next section).

Before each CO_2 flux measurement, the Tygon® tubes exiting the chamber were fitted with autoshutoff Quick Couplings™ (Colder Products Company, USA), and the CO_2 contained within the sampling system is removed using the CO_2 scrubber cartridge. When no CO_2 is left in the sampling system (as indicated by the IRGA), the air flow is diverted through the bypass, 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, pCO_2 in the chamber is lowered to near atmospheric pCO_2 by guiding the air flow through the CO_2 scrubber cartridge. We let the CO_2 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 pCO_2 measurements into the mass of carbon contained in the chamber:

$$m = \frac{pCO_2}{10^6} \cdot V \cdot A \quad (4)$$

where m is the mass of carbon in the chamber (in mgC), pCO_2 the concentration of CO_2 in the chamber in ppm ($cm^3.m^{-3}$), V is the total volume (cm^3) i.e., the sum of the volume of the chamber (V_{CH}) and the volume of the CO_2 sampling system (V_L) when air flows through the bypass. Factor A converts centimetres cubed of CO_2 into milligrams of carbon, depending on temperature and pressure following the ideal gas law:

$$A = \frac{P \cdot M_C}{R \cdot T} . 10^{-3} \quad (5)$$

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 ($m^3.Pa.K^{-1}.mol^{-1}$) 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 $gC.m^{-2}.yr^{-1}$) emitted to the atmosphere under the form of CO_2 using:

$$Q = \frac{q}{S} \cdot 525.6 \quad (6)$$

where, 525.6 converts $mgC.min^{-1}$ into $gC.yr^{-1}$, and S (m^2) 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):

$$\frac{dm(t)}{dt} = q - \lambda(m(t) - m_0) \quad (7)$$

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 CO_2 accumulation and that should be close to the mass of carbon in the chamber at atmospheric pCO_2. 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 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 CO_2 flux in soils, the curvature (λ) relates to leakages, diffusivity from soil CO_2 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):

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

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^{-1} for 20 seconds was empirically found suitable; Figure 3B).

Several parameters lead to uncertainties on the flux calculations. They are all related to the conversion of pCO_2 to mass of carbon (Table 1): i) the volume of the chamber (V_{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 cm^3 through an experiment of successive CO_2 dilution in a known volume); and iv) the temperature in the chamber was assumed to range from 0 to 20ºC 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 CO_2 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 ± 2.7 %. In the case that the relative standard deviation on multiple flux measurements is higher than 2.7%, we adopt the standard deviation as the uncertainty.

2.4 CO_2 sampling and isotopic analysis

CO_2 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 H_2O and CO_2, and are widely used to separate CO_2 from air at ambient temperature and pressure. The gas trapped by the zeolite sieve can be extracted in the laboratory at high temperature for CO_2 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 CO_2 was sampled 'actively' – i.e., using the CO_2 sampling system coupled to the

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 CO_2 onto the trap can be controlled to return the chamber to ambient atmospheric pCO_2, allowing for a subsequent measurement of CO_2 flux (Figure 3). The second approach allows pCO_2 to accumulate in the chamber, before attaching the scrubbed line and removing the CO_2, which we tested on 30/03/2017. The 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 previous work (Garnett et al., 2009; Garnett and Hardie, 2009), it is expected that the passive trap method can lead to an isotope fractionation of $\delta^{13}C \sim 3.50 \pm 0.45$ ‰ associated with the diffusion of CO_2 from the chamber to the zeolite trap. In addition, a sample of local atmospheric CO_2 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 for CO_2 recovery. The CO_2 collected was desorbed from the zeolite by heating (425ºC) and cryogenically purified (Garnett and Murray, 2013). One aliquot of the recovered CO_2 was used for $\delta^{13}C$ measurement using Isotope Ratio Mass Spectrometry (IRMS; Thermo Fisher Delta V; results expressed relative to the VPDB standard). A further aliquot was converted to graphite and analysed for ^{14}C using accelerator mass spectrometry at the Scottish Universities Environmental Research Centre. Radiocarbon results 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) [Stuiver and Polach (1977); corresponding to $^{14}a_N$ in Mook and van der Plicht (1999), or $F^{14}C$ in Reimer et al. (2004)] (Table 2).

2.5 Partitioning the sources of CO_2

As the chamber was were drilled away from the obvious influence of root respiration, the CO_2 emanating 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 (see discussion below). To correct for possible atmospheric contamination, and partition the sources of CO_2, we solve the following isotope-mass balance system:

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$$\begin{cases} f_{Atm} + f_{Rock\,OC} + f_{Carb} = 1 \\ f_{Atm} \cdot \delta^{13}C_{Atm} + f_{Rock\,OC} \cdot \delta^{13}C_{Rock\,OC} + f_{Carb} \cdot \delta^{13}C_{Carb} = \delta^{13}C_{Chamber} \\ f_{Atm} \cdot Fm_{Atm} + f_{Rock\,OC} \cdot Fm_{Rock\,OC} + f_{Carb} \cdot Fm_{Carb} = Fm_{Chamber} \end{cases} \quad (9)$$

where, f_{Atm} is the mass fraction of CO_2 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 CO_2 sampled from the chambers and extracted from the zeolite molecular sieves.

The $\delta^{13}C$ composition (vs. VPDB) of the rock-derived organic carbon was obtained by IRMS after inorganic carbon removal from the rock powdered samples by HCl fumingation, followed by closed-tube combustion to produce CO_2. The $\delta^{13}C$ composition of the carbonates 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 contain radiocarbon levels close to the AMS background (Table 3).

3 Results and Discussion

Here we present the results obtained from a natural weathering chamber (H6) drilled in December 2016. Our aim is to assess the feasibility of the method, in terms of: i) measuring the fluxes of CO_2; ii) collecting sufficient mass of CO_2 for isotope analysis (to partition between organic and inorganic derived CO_2); and iii) checking the role of atmospheric CO_2 contamination for both the active and passive CO_2 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 CO_2 release.

3.1 Flux Measurements

Three months after the installation of the chamber H6, CO_2 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 ($\frac{dm(t)}{dt}$) 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 pCO_2 gradient between the chamber and the atmosphere. Since this gradient is positive in the chamber (Figure 2) ($pCO_{2_{chamber}} > pCO_{2_{atmosphere}}$), then CO_2 likely diffuses from the chamber to the atmosphere. This has the advantage that it naturally minimizes any atmospheric CO_2 contamination. Conversely, since the CO_2 production is linked to the consumption of O_2, then the O_2 gradient is expected to be negative ($pO_{2_{chamber}} < pO_{2_{atmosphere}}$), and thus atmospheric O_2 naturally diffuses inside the chamber. This means that the chamber can be closed for months and still contain gaseous O_2. Our measurements of O_2 using the EGM-5 O_2 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).

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The fluxes of CO_2 measured in this chamber on 27/03/2017 decreased from 529 ± 14 $gC.m^{-2}.yr^{-1}$ to 266 ± 7 $gC.m^{-2}.yr^{-1}$ with the number of times we extracted the CO_2 from the chamber (Figure 3). The flux becomes approximately constant after three CO_2 extractions during zeolite trapping, with an average of 272 ± 8 $gC.m^{-2}.yr^{-1}$ (1sd, n=4) for the last 4 repeats (Figure 3). This observation might be explained by the fact that over time (days to months), CO_2 accumulates not only in the chamber, but also in the rock pores 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. When CO_2 is first extracted from the chamber, the CO_2 stored in the surrounding pores quickly refills the chamber. It appears that after three extractions this CO_2 is depleted, meaning that the more constant values correspond to the actual flux of CO_2 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 CO_2. It remains to be seen the degree to which this feature is widespread, or chamber specific.

3.2 Isotope measurements

The atmospheric CO_2 was sampled on 27/03/2017, yielding a $\delta^{13}C$ of -9.6‰ and a ^{14}C activity of Fm=1.0065±0.0044. From chamber H6, we sampled CO_2 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 ^{14}C activities (Fm of 0.0597±0.0047 and 0.0562±0.0047, respectively) were identical within measurement uncertainty. Because the CO_2 originating from rock-derived organic matter and carbonate minerals is '^{14}C-dead', as confirmed by ^{14}C measurements of the organic carbon and carbonate of the rock from the studied chamber (Table 3), the atmospheric CO_2 input can be calculated as $100 \times \frac{Fm_{Chamber}}{Fm_{Atm}}$ %. The Fm from both samples show that only ~5.5% to 6% of the CO_2 trapped was of atmospheric origin and that the two active trapping methods produce comparable results. The $\delta^{13}C$ 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. The difference may reflect different relative rates of sulphide versus organic matter oxidation over a daily timescale, which is an observation worth exploring in more detail.

From chamber H6, the CO_2 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 CO_2 (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 CO_2 (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 CO_2. This is perhaps surprising since the trap was left exposed in the natural environment for three months. However, it results from the high pCO_2 present in the chamber throughout the time period, driving a net diffusive transfer of CO_2 from chamber to the zeolite sieve. It suggests the components used to make the chamber and its linkages are not susceptible to major leaks.

The $\delta^{13}C$ composition of the passively trapped CO_2 was -9.4‰, displaying a 2.0‰ and 3.3‰ depletion when compared to the $\delta^{13}C$ values obtained with the active trapping method. This suggests that fractionation during passive trapping occurred, in

agreement with 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 CO_2 through air (Davidson, 1995).

We solve the isotope-mass balance Eq. (9) for the actively trapped CO_2 from 27/03/2017 and 30/03/2017, and for the passively trapped CO_2 sample (Table 4). The $\delta^{13}C$ of the passively trapped CO_2 was corrected using the published 3.50 ± 0.45‰ fractionation factor (Garnett et al., 2009; Garnett and Hardie, 2009), and the ^{14}C activity of both the rock-derived organic carbon and carbonate end-member were set to 0, as their measured Fm were close to background (Table 3). We found very similar results for the three trapped CO_2 samples, yielding 5% to 6% of CO_2 from atmospheric contamination, 71% to 77% of CO_2 from the dissolution of the carbonates by sulphuric acid and 19% to 23% of CO_2 from the oxidation of rock-derived organic matter (details in Table 4).

A correction for the ingress of atmospheric CO_2 is applied to partition the measured flux of CO_2. This shows 19% to 24% from rock-derived organic carbon and 76% to 81% from carbonate dissolution (Table 4). Therefore, for chamber H6 on 27/03/2017 for which we simultaneously measured the bulk CO_2 flux (272 ± 8 $gC.m^{-2}.yr^{-1}$), these proportions equate to a flux of 66 ± 2 $gC.m^{-2}.yr^{-1}$ derived from the natural oxidation of rock organic matter, and a flux of 206 ± 6 $gC.m^{-2}.yr^{-1}$ 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 116 grams of rock would be weathered by sulphuric acid to produce the carbonate-derived CO_2 flux (i.e., 7.6 gC produced in one year from a rock with 6.52 w% of inorganic carbon). In contrast, 2210 grams of sedimentary rock would need to have been oxidized to produce the rock-organic carbon CO_2 flux (i.e., 2.4 gC 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. The oxidation of organic carbon appears to occur more homogeneously in the rock mass.

3.3 Natural flux of CO_2 evading sedimentary rocks

3.3.1 Rock-derived organic carbon oxidation

The flux of CO_2 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 CO_2 and its isotopes in Saskatchewan (Canada) (Keller and Bacon, 1998). This is 130 times lower than our estimate in the chamber H6 of the Laval catchment. 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 exposes rocks to oxidative weathering (Graz et al., 2012).

CO_2 fluxes derived from the oxidation 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) (66 ± 2 $gC.m^{-2}.yr^{-1}$) are of the same order of magnitude as that calculated in highly erosive Taiwanese catchments (5 to 35 $gC.m^{-2}.yr^{-1}$) (Hilton et al., 2014). It is clearly too early to directly relate these fluxes. It is likely that individual chambers have different CO_2 fluxes (possibly depending on rock heterogeneity, temperature, water supply),

and that CO_2 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 CO_2 flux measured during our experiment (206 ± 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 CO_2 to the atmosphere. A study reporting the average anion concentrations in the Laval stream in 2002 (Cras et al., 2007) gives a low bicarbonate-to-sulphate ratio ($\frac{HCO_3^-}{SO_4^{2-}} \sim 0.35$). 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 CO_2 (Eq. (2), i.e., $\frac{HCO_3^-}{SO_4^{2-}} = 0$) instead of dissolved inorganic carbon (Eq. (3), i.e, $\frac{HCO_3^-}{SO_4^{2-}} = 2$) at the weathering site. Because carbonate minerals are highly reactive, this means that the sulphuric acid weathering of carbonate minerals could produce a local CO_2 flux which starts to approach the rates of respiration in modern soils (e.g., Pirk et al. 2016).

The published river ion data can be used to estimate the weathering of carbonate minerals by sulphuric acid. From the average Ca^{2+} and SO_4^{2-} concentrations measured in 2002 and the average runoff (Cras et al., 2007), assuming that the weathering of carbonates produced only gaseous CO_2, we estimate a flux of CO_2 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 SO_4^{2-} to partition sulphate source (Calmels et al., 2007). Although of the same order of magnitude, the 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.

Our local direct measurement is higher than the flux obtained for a similar highly erosive catchment in Taiwan (Liwu River) using dissolved river chemistry and showing a value of ~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 the strong 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 CO_2 production by this weathering process.

4 Conclusions

Here, we present a reliable, innovative and relatively inexpensive way to measure the flux of CO_2 produced during the oxidative weathering of sedimentary rocks. The ability to trap the CO_2 using active or passive zeolite molecular sieves is essential, since

its carbon isotopic composition (^{12}C, ^{13}C, ^{14}C) is mandatory to assess for atmospheric CO_2 inputs, before partitioning the CO_2 flux between that from oxidation of rock-derived organic carbon and carbonate dissolution by sulphuric acid. The passive method to trap the CO_2, i.e., leaving zeolite molecular sieve connected to a chamber for days to months, is useful to provide a time integrative sample of CO_2 produced during weathering. This paper is a proof of concept of the oxidative weathering of rocks: i) rock-derived organic carbon is oxidized and CO_2 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. In the Laval catchment this phenomenon releases CO_2 directly to the atmosphere rather than dissolved inorganic carbon, and its flux can be locally large.

Data availability

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

Author contribution

RGH conceived the research and designed the study with GS and MHG. GS, RGH and SK carried out chamber installation. 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)

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

[b]Given as ranges: median (min - max)

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 composition of the rock sampled during the drilling of chamber H6[a]

	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	-30.8 ± 0.1	0.0125 ± 0.0039

[a]in 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 ($gC.m^{-2}.yr^{-1}$)
DRA16-H6-1512-P	SUERC-73091	Passive[a]	Atmosphere	4.9 ± 0.5	–	–
			Carbonates	76.7 ± 1.5	80.7 ± 1.6	–
			Rock Organic Carbon	18.4 ± 1.5	19.3 ± 1.6	–
DRA17-H6-2803-A	SUERC-73096	Active	Atmosphere	5.9 ± 0.5	–	–
			Carbonates	71.2 ± 0.5	75.7 ± 0.4	206 ± 6[b]
			Rock Organic Carbon	22.9 ± 0.4	24.3 ± 0.4	66 ± 2[b]
DRA17-H6-3003-A	SUERC-73094	Active	Atmosphere	5.6 ± 0.5	–	–
			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 $\delta^{13}C$ of the passive sample was corrected for a fractionation factor of 3.50 ± 0.45 (Garnett et al., 2009)

[b] from a measured bulk CO_2 flux of 272 ± 8 $gC.m^{-2}.yr^{-1}$

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Figures

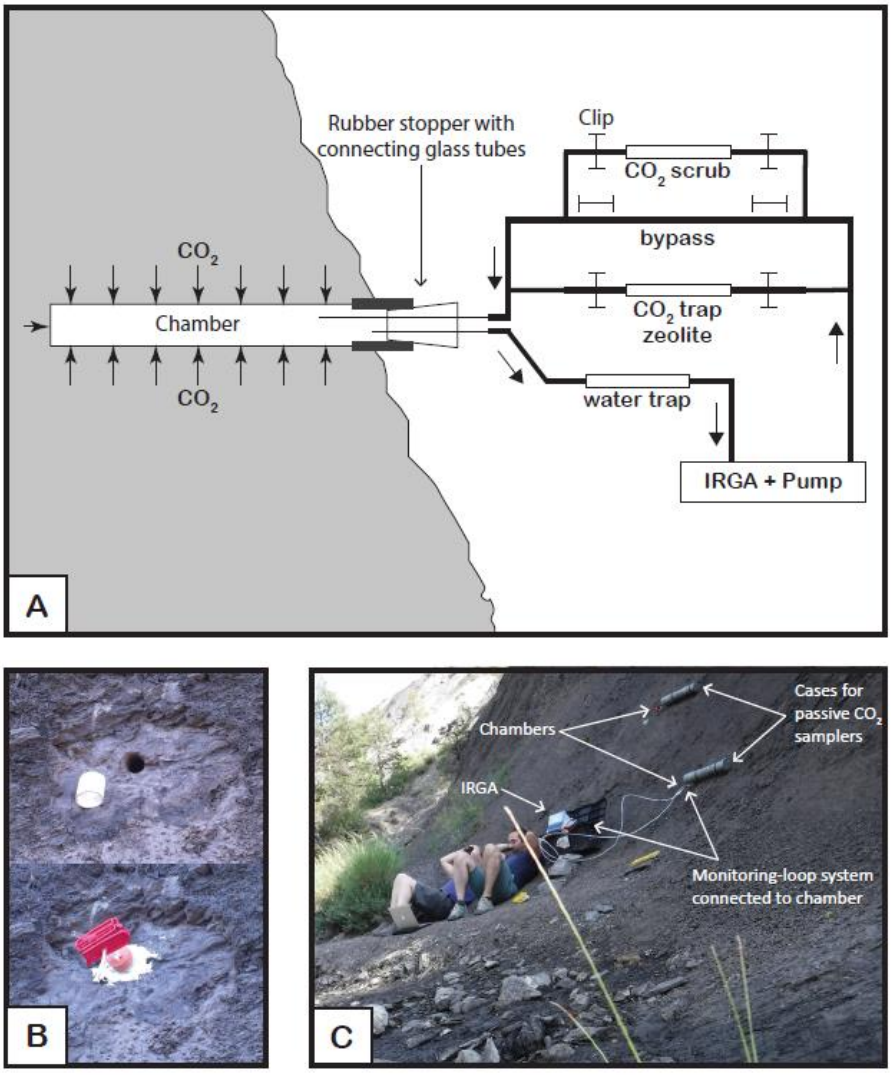

Figure 1: A: Schematic diagram of the closed-loop monitoring-sampling system connected to the natural weathering chamber. Gas flow pathways are controlled by opening and closing the clips. Clips removed from the bypass allow pCO_2 in the chamber to be monitored (IRGA stands for Infra-Red Gas Analyzer), thus measuring CO_2 flux and ensuring that enough CO_2 accumulated in the chamber for ^{14}C analysis. To remove CO_2 from the line before connecting to the chamber, clips are moved from the CO_2 scrub (soda lime). When connected to the chamber, the CO_2 scrub can be used to lower the CO_2 concentration before flux measurement. To collect CO_2 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 tubing 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 passive CO_2 trapping.

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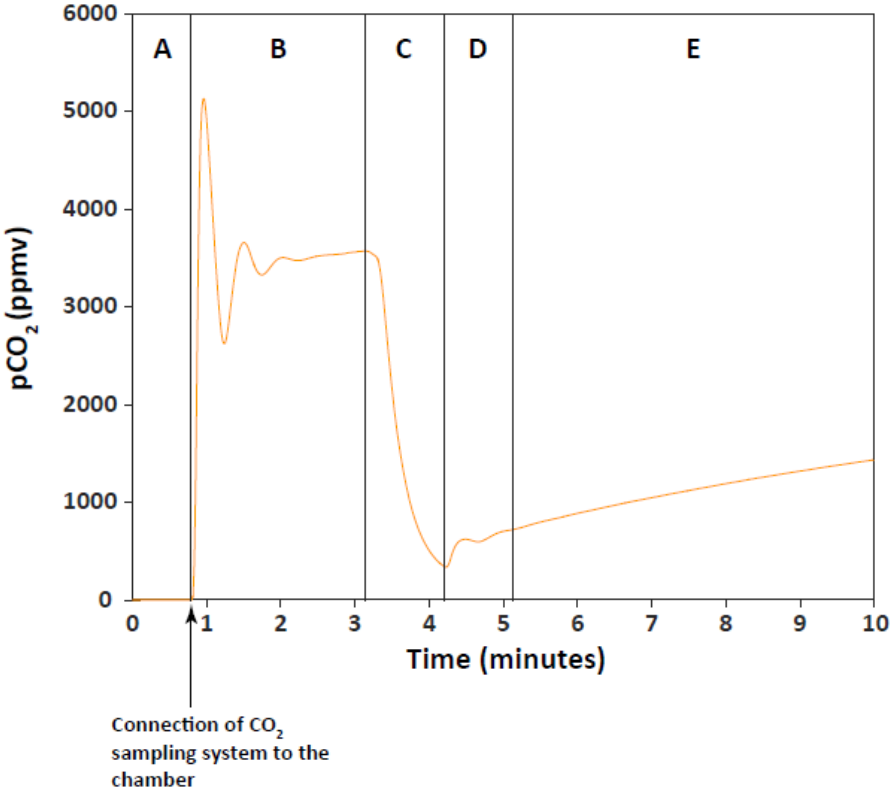

Figure 2: An example of the monitoring of the CO_2 accumulating in a chamber. The orange curve is the partial pressure of CO_2 (pCO_2, in parts per million volume) through time in chamber H6 on 27/03/2017. A: The CO_2 sampling-monitoring system is not connected to the chamber. Atmospheric CO_2 has been removed from the system (pCO_2 = 0 ppm) using the CO_2 scrub cartridge. B: The closed-loop monitoring system has been connected to the chamber. pCO_2 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 CO_2 sampling-monitoring system) which decreases pCO_2 and requires some time for the pCO_2 to equilibrate. We determined that when connected to the chamber, the maximum value of pCO_2 read is 0.94 the actual pCO_2 in the chamber. C: The CO_2 in the chamber is lowered (scrubbed with the CO_2 scrub, or trapped with the zeolite molecular sieve) to near atmospheric pCO_2. D: residual CO_2 that in the chamber homogenized with the rest of the total volume "artificially" increasing pCO_2 quickly. E: pCO_2 in chamber is monitored, reflecting the flux of CO_2 from the rock surface to the chamber.

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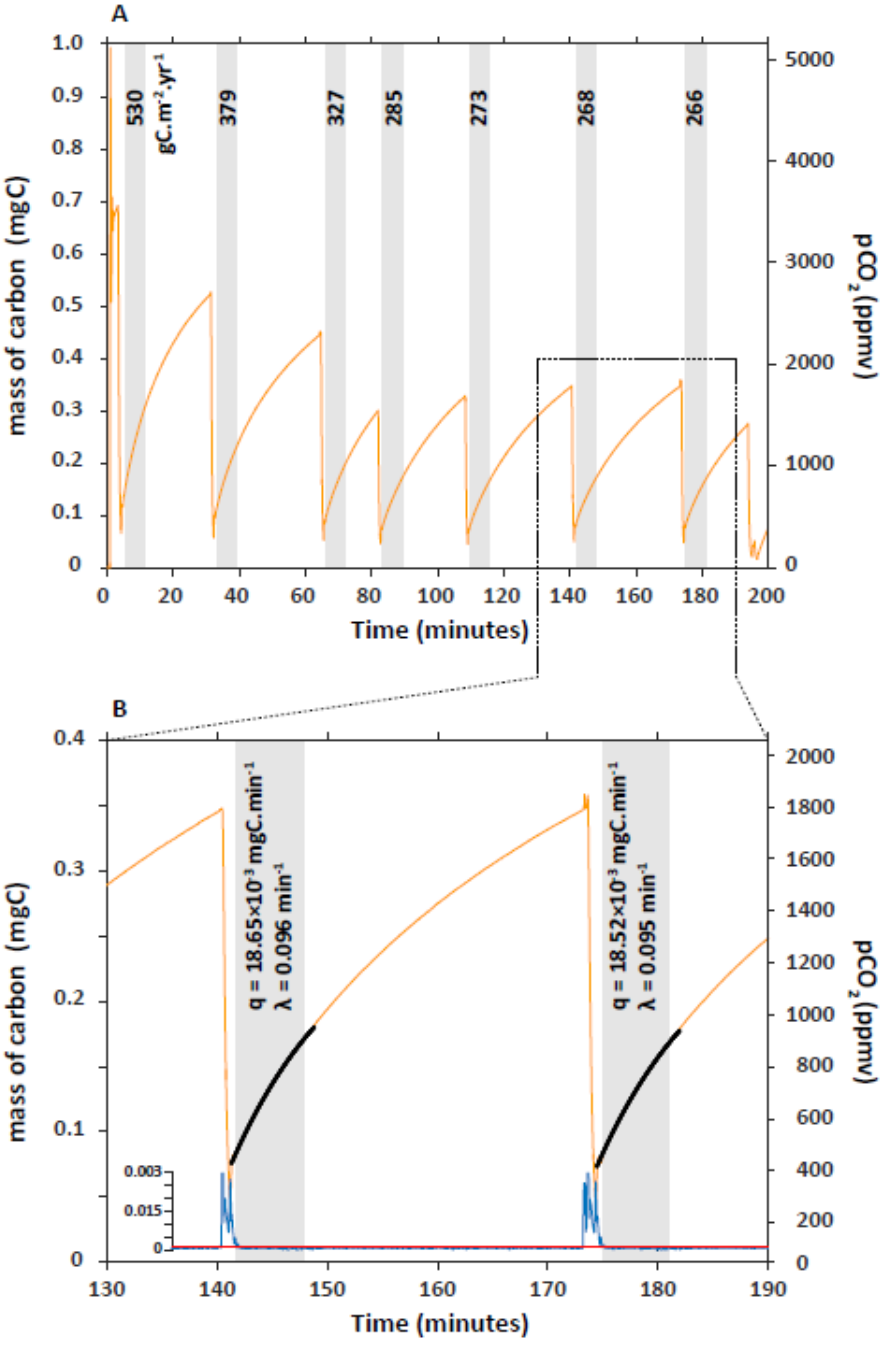

Figure 3: A: Series of carbon flux measurements for chamber H6 on 27/03/2017. CO_2 concentration (pCO_2) was converted into mass of carbon (mgC) following Eq. (4) and Eq. (5). Flux of CO_2 – the numbers associated to shaded boxes – are given in $gC.m^{-2}.yr^{-1}$. B: Close–up of how fluxes were calculated 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-sec moving window variability in the rate of mass carbon change (blue curve) was below a threshold of 10^{-4} $mgC.min^{-1}$ (red line).

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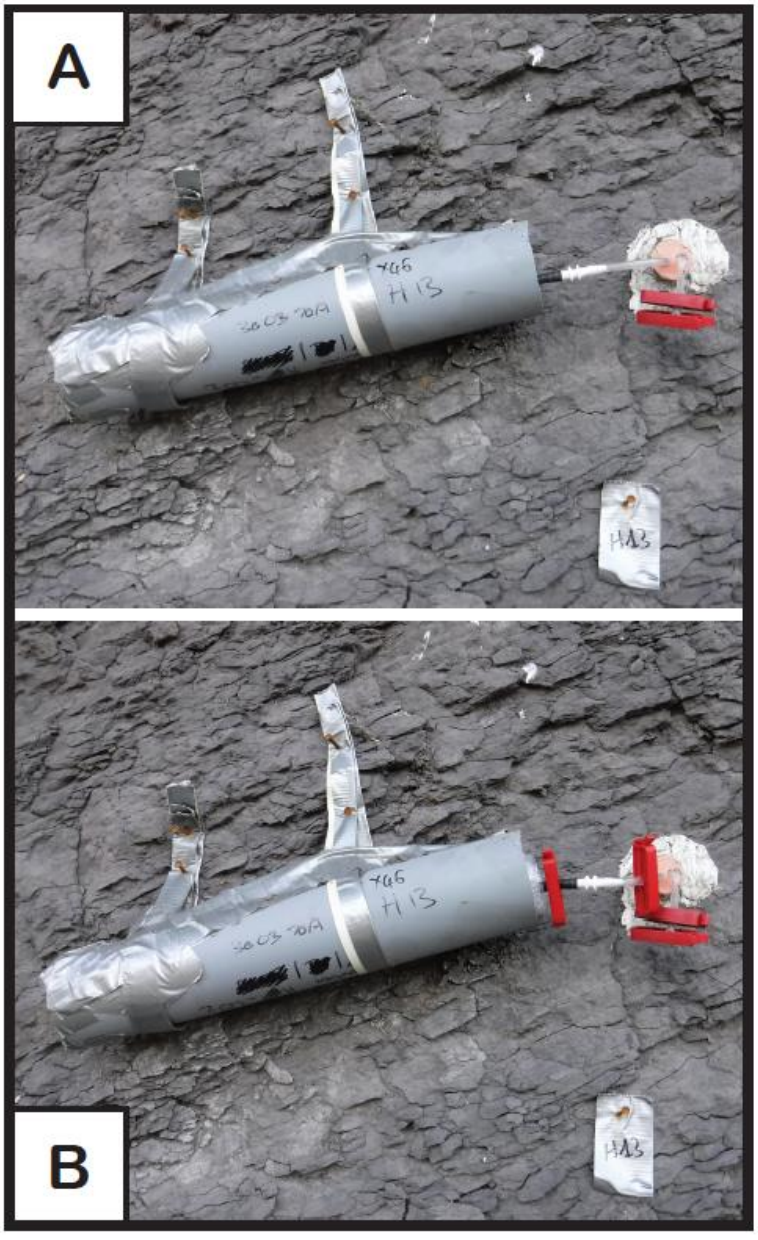

Figure 4: A: Zeolite molecular sieve connected to a chamber for passive CO_2 trapping. The zeolite molecular sieve is encased in the grey PVC tubing and connected for months to the chamber using a white connector. B: Zeolite molecular sieve ready to be disconnected from chamber. The red clips are positioned so that they seal both the zeolite molecular sieve and the chamber.