

Temperature control on CO₂ emissions from the weathering of sedimentary rocks

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Abstract

Sedimentary rocks can release carbon dioxide (CO₂) during the weathering of rock organic carbon and sulfide minerals. This sedimentary carbon could act as a feedback on Earth's climate over millennial to geological timescales, yet the environmental controls on the CO₂ release from rocks are poorly constrained. Here, we directly measure CO₂ flux from weathering of sedimentary rocks over 2.5 years at the Draix-Bléone Critical Zone Observatory, France. Total CO₂ fluxes approached values reported for soil respiration, with radiocarbon analysis confirming the CO₂ source from rock organic carbon and carbonate. The measured CO₂ fluxes varied seasonally, with summer fluxes five times larger than winter fluxes, and were positively correlated with temperature. The CO₂ release from rock organic carbon oxidation increased by a factor of 2.2 when temperature increased by 10°C. This temperature sensitivity is similar to that of degradation of recent-plant-derived organic matter in soils. Our flux measurements identify sedimentary rock weathering as a positive feedback to warming, which may have operated throughout Earth's history to force the surface carbon cycle.

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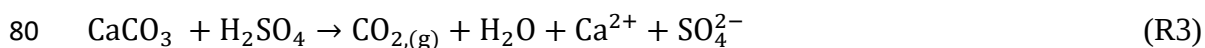
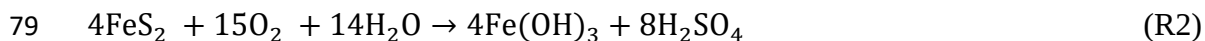
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68 **Main text**

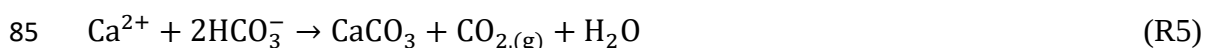
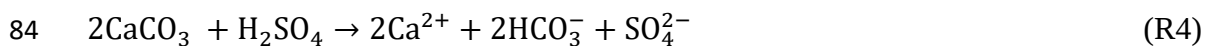
69 Sedimentary rocks contain vast stores of carbon in the form of organic carbon (rock-derived
70 OC, or OC_{petro}) and carbonate minerals (for example calcite; CaCO₃), equating to 130,000 times
71 that of the pre-industrial atmosphere¹. When exhumation and erosion expose sedimentary rocks
72 to the atmosphere and hydrosphere^{2,3}, oxidative weathering processes can release CO₂ through
73 three main pathways. The oxidation of OC_{petro} by atmospheric dioxygen (O₂) (ref. ^{4,5}) leads to
74 CO₂ emissions to the atmosphere:



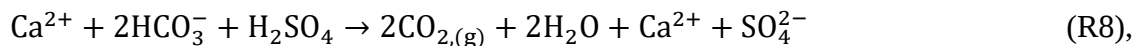
76 The second pathway is via the oxidation of sulfide minerals (FeS₂; e.g. pyrite) which produces
77 sulfuric acid (H₂SO₄). This can dissolve carbonate minerals and release CO₂ immediately to
78 the atmosphere (ref. ⁶⁻⁸):



81 Alternatively, the carbon can enter the bicarbonate pool of rivers and be transferred to the
82 ocean. The CO₂ release to the atmosphere is then delayed by an order of 10⁴ years, i.e., the
83 timescale of the carbonate precipitation in the ocean^{6,9}:



A third pathway of CO₂ release from rock can occur following the weathering of carbonate by carbonic acid (H₂CO₃), produced by the dissolution of atmospheric CO₂ in meteoritic water⁶, followed by the addition of sulfuric acid to that dissolved inorganic carbon pool:



where one mole of the resultant CO₂ release derives from carbonate.

The global fluxes of CO₂ from sedimentary rock weathering are key players in the geological carbon cycle³. Sedimentary rocks dominate Earth's near surface, covering ~64% of the continental area¹⁰ and store an estimated 1.1 x 10⁶ megatonnes (10¹² grams, MtC) of OC_{petro} in the upper 1 m alone¹¹. Chemical weathering is estimated to release 40 – 100 MtC.y⁻¹ by OC_{petro} oxidation (ref. ¹²). The co-occurrence of sulfide and carbonate minerals is less well known, as are the global weathering fluxes, but ~31-36 MtC.y⁻¹ is estimated to be released from sulfide oxidation coupled to carbonate dissolution^{9,13}. These CO₂ emissions are similar to the 79 ± 9 MtC.y⁻¹ released by volcanism¹⁴.

While the global fluxes are known to be important, the sensitivity of CO₂ emissions from sedimentary rock weathering to climate (temperature and hydrology) remains unconstrained. OC_{petro}, in particular, has been previously viewed as relatively unreactive in the weathering zone¹⁵. Most of our insight on the patterns and controls on CO₂ emissions from oxidative weathering come from studies of geochemical tracers dissolved in river waters^{6,7,16–18}. These studies have highlighted the important role of erosion, which supplies OC_{petro} and sulfides to the near-surface zone of oxidative weathering, for setting the rates of CO₂ release^{7,17,19}. However, these indirect estimates average over catchment areas that integrate

reactions operating under variable hydrologic and temperature conditions. For instance, recent work has highlighted that historical increases in sulfate fluxes in alpine rivers could reflect sulfide oxidation responding to warming, but direct evidence was lacking²⁰. To move forward, we use a newly designed method which allows the release of CO₂ during sedimentary rock weathering to be measured directly at the scale of the outcrop²¹. We directly measure, for the first time, monthly to annual variability in CO₂ fluxes from oxidative weathering of rocks, allowing us to constrain how they are moderated by changing temperature.

New measurements of rock weathering and CO₂ release

We installed five rock chambers (Fig. 1, Methods) in December 2016 in the Laval catchment (0.86 km²) of the INRAE Draix-Bléone observatory, France, an OZCAR Critical Zone Observatory^{22,23} with four decades of measurements of physical (e.g., river solid load), chemical (e.g., river dissolved chemistry) and meteorological (e.g., air temperature, rainfall, river discharge) parameters^{22,24,25}. The catchment is composed of Jurassic marls that have features that are likely to be widespread in shales and other sedimentary rocks: they are bedded on the centimetre scale²⁶ and fractured at the decimetre-to-meter scale²⁷; and they contain OC_{petro} concentrations of ~0.5 w% (ref. ²⁵ and Supplementary Table 1), which is lower than a global compilation of Phanerozoic shales, with OC_{petro} ~1 to 3 w% (ref. ²⁸); and they have undergone moderate thermal maturation at temperatures not exceeding 410°C (ref. ²⁹). The marls also contain sulfide minerals²⁹ (~0.6 w% sulfur; Supplementary Table 1), and high concentrations of carbonate minerals (~45 w%; Supplementary Table 1). In this catchment, bare rock outcrops over 68% of the catchment surface area and a combination of steep slopes, frost-shattering in winter months, intense rainfall during storms and finely bedded rocks lead to high erosion rates of 7 to 10 mm.year⁻¹ (ref. ^{21,22,25}) which are characteristic of many steep, sedimentary-rock dominated catchments³. Previous work²⁴ has established that the Laval stream has a low bicarbonate to sulfate ion ratio of ~0.35, indicating widespread sulfide

oxidation, and suggesting CO₂ emissions through carbonate weathering via reactions (R3) and (R7-8).

To establish the environmental controls on sedimentary rock weathering, we measured CO₂ emissions in rock chambers (Methods) on seasonal visits for 2.5 years from December 2016 to May 2019. The CO₂ was sampled using zeolite molecular sieves, following an active CO₂ trapping method²¹ (Methods). The stable carbon isotopes ($\delta^{13}\text{C}$) and radiocarbon activity ($F^{14}\text{C}$) of CO₂ were measured to fingerprint its source²¹. The $F^{14}\text{C}$ of CO₂ was generally low, confirming a geological source (OC_{petro} and carbonates) from the weathering of marls (Reactions. R1, R3 and R7, Fig. 2). The chambers were installed on bedrock outcrops devoid of recent soil organic matter and with no evidence for root penetration (Fig. 1a). The presence of ^{14}C in the CO₂ samples can result from the input of atmospheric CO₂ to a dissolved inorganic carbon pool via the carbonic acid weathering of carbonate (Reaction R7-8), and/or minor leaks from the atmosphere during sampling (Methods).

The measured total CO₂ fluxes derived from pyrite oxidation combined to carbonate dissolution pathways (Reactions R3 and R7-8) plus OC_{petro} oxidation (Reaction R1) in the Laval catchment approach those of soil respiration³⁰ (Extended Data Fig. 1). We note caution in upscaling these values, as the volume of rock porosity that has been captured could vary between chambers. The total CO₂ fluxes displayed temporal and spatial variability (Fig. 3a): at chamber H6, fluxes varied between 270 mgC.m⁻².day⁻¹ in December 2016, to 3040 mgC.m⁻².day⁻¹ in October 2017 (Fig. 3a). Changes in the CO₂ flux showed a marked seasonal pattern, with warm months characterized by higher CO₂ fluxes (Fig. 3a). CO₂ emissions measured at chamber H4 – located one metre below chamber H6 – were always lower than H6 (Fig. 3a).

Temperature and hydrological controls on CO₂ release

We found a common temperature response to the rock-derived CO₂ emissions across our chambers. For each chamber, the measured total CO₂ flux was positively correlated to the

daily-averaged temperature measured in the chamber (Methods) through a growth exponential model (Fig. 4a and Supplementary Table 2):

$$F = F_0 \times \exp (\alpha T) \quad (1),$$

where, F is the CO_2 flux (in $\text{mgC.m}^{-2}.\text{d}^{-1}$), T is the temperature in the chamber (in $^{\circ}\text{C}$), F_0 is the amplitude (or the CO_2 flux at 0°C), α is the growth rate parameter (in $^{\circ}\text{C}^{-1}$). The growth rate parameter α is similar for each chamber, with values ranging from 0.057 to $0.079^{\circ}\text{C}^{-1}$ (Supplementary Table 2). When we normalise the measured CO_2 flux to the amplitude parameter (F/F_0), the five chambers reveal a coherent seasonal pattern in the CO_2 flux: on average, summer fluxes (June-July-August) are five times larger than winter fluxes (December-January-February) (Fig. 4b). Using the normalized flux data from five chambers over 2.5 years, the growth rate parameter α is $0.070 \pm 0.007^{\circ}\text{C}^{-1}$ (Fig. 4b and Supplementary Table 2).

The absolute total CO_2 fluxes (Fig. 3a-4a) and the amplitude parameter (F_0) vary between chambers despite their close proximity (Fig. 1, Methods), with F_0 between 35 and $626 \text{ mgC.m}^{-2}.\text{d}^{-1}$ (Supplementary Table 2). The F_0 value is positively correlated with the elevation of the chamber above the Laval river bed ($r^2 = 0.98$; $n = 5$; Fig. 5), suggesting the absolute total fluxes relate to the relative position of the chamber above the water table. At higher elevations, diffusion of gaseous O_2 into the rock may promote oxidation of pyrite and OC_{petro} and gaseous CO_2 can diffuse out of the rock face. Closer to the water table, water-filled pores may slow down diffusion of gaseous O_2 and CO_2 , reducing the OC_{petro} oxidation and carbonate dissolution by sulfuric acid (Reactions R1 and R3), while also exporting some carbon as dissolved inorganic carbon to the river^{31,32}. However, as carbonic acid is supplied by infiltrating water, carbonate dissolution by the carbonic acid pathway (Reaction R7) may be predominant closer to the water table, although still limited by the presence of sulfuric acid to degas CO_2 (Reaction R8). O_2 diffusion in gas/water-filled pores³³ has been invoked at other field sites to

explain the location of pyrite and carbonate weathering fronts³⁴ and the OC_{petro} oxidation front⁴ close to the water table.

Based on these concepts invoked to explain the pattern in absolute fluxes across the chambers (Fig. 5), some of the variability in the CO₂ fluxes at a given chamber (Fig. 3-4) could be linked to precipitation, infiltration and runoff before or during measurements. Indeed, we see this during repeated measurements of H6 and H4 between 10/04/2019 to 10/05/2019, which experienced six short rainfall events that increased the Laval stream discharge (Extended Data Fig. 2). Each rainfall event reduced CO₂ fluxes, but they recovered over a few days (Extended Data Fig. 2). In contrast, the largest CO₂ flux occurred in mid-October 2017 after a 4-month period of drought (Fig. 3a, Extended Data Fig. 3). All chambers showed similar responses to hydrological forcing, suggesting that gas motion – into the rock for O₂, and out of the rock for CO₂ – is modulated by the degree of water saturation^{4,34}. Lateral export of CO₂ as dissolved inorganic carbon^{31,35} may also play a role in the CO₂ flux variability we observed. However, it cannot explain the seasonal pattern of the total CO₂ flux over 2.5-years, nor the correlation with temperature. Indeed, the near surface water content of the marls in the Laval catchment³⁶ is not correlated with temperature (Extended Data Fig. 4), while a month-long detailed measurements clearly shows that CO₂ emissions closely follow daily-averaged chamber temperature (Extended Data Fig. 2).

Temperature sensitivity and wider implications

The overall sensitivity of rock weathering and total CO₂ emissions to temperature is provided by the average growth exponential value α ($0.070 \pm 0.007 \text{ }^{\circ}\text{C}^{-1}$) of the whole data set (Fig. 3b). This value can be used to calculate a Q₁₀ factor, by which the oxidative weathering processes responsible for the CO₂ flux change as a result of a 10°C rise in temperature:

$$Q_{10} = \exp(10\alpha) \quad (2)$$

In the Laval catchment, total CO₂ release during rock weathering responds to temperature with a Q₁₀ factor of 2.0 ± 0.1 over the range 0-25°C. This value is “apparent” as it is the integrated response of many biogeochemical processes, constrained by field conditions^{37,38}.

To explore this temperature sensitivity further, we partition the total fluxes into carbonate-derived (Reaction R3 and Reactions R7-8) and OC_{petro}-derived (Reaction R1) CO₂ using $\delta^{13}\text{C}$ and F¹⁴C values of the CO₂ sampled in the chambers (Methods). This assumes that ¹⁴C measured in the CO₂ samples comes from atmospheric CO₂ via its dissolution as carbonic acid in rainwater (Reaction R6), which weathers carbonate as it infiltrates the shallow subsurface (Methods). In chamber H6, an average of 22 ± 6 % of the CO₂ is sourced from OC_{petro} oxidation (Reaction R1), 60 ± 6 % from CaCO₃ dissolution by sulfuric acid (Reaction 3), and 18 ± 9 % from CaCO₃ dissolution by carbonic acid (Reactions R7-8). The relatively low bicarbonate to sulfate ion ratio (~ 0.35) in the Laval stream water²⁴ supports that the CaCO₃ dissolution derived mostly by sulfide oxidation via H₂SO₄ following Reaction (R3), or coupled to H₂CO₃ following Reactions (R7-8). For chamber H4, the relative proportion of OC_{petro} is lower (4 ± 4 % of the total CO₂), as is the relative proportion of CO₂ produced by carbonate-dissolution by sulfuric acid (50 ± 6 %). In contrast, the proportion of H₂SO₄-induced CO₂ degassing from the dissolved inorganic carbon pool is larger (46 ± 8 %). These contrasts between H4 and H6 are intriguing, but it is difficult to draw definitive conclusions from two chambers. However, they suggest that the near-surface hydrological setting could influence the magnitude of CO₂ release (Figure 5), its short-term temporal variability (Extended Data Fig. 2) and the ultimate pathway that carbon takes from rocks to the atmosphere.

The CO₂ fluxes sourced from OC_{petro} and carbonate both vary seasonally and are positively correlated with temperature in chamber H6 (Supplementary Table 3). Over the 0-25°C range, the Q₁₀ factor for sulfide oxidation coupled to carbonate dissolution is 1.7 ± 0.3 ($R^2 = 0.31$, p-value < 0.001, n = 27). This supports inferences from changing SO₄²⁻

concentrations of stream water in response to temperature in alpine settings²⁰. The apparent activation energy (Ea) for this process is $48 \pm 12 \text{ kJ.mol}^{-1}$ ($R^2 = 0.53$, p-value < 0.002 , $n = 18$) for H6, which is lower than $\sim 90 \text{ kJ/mol}$ reported from experimental abiotic oxidation of pyrite at circumneutral pH (ref. ³⁹). The lower Ea we observed here in natural settings suggests that biologic processes may play a role in accelerating the kinetics of sulfide oxidation^{7,40} during rock weathering. Importantly, we show that the corresponding CO₂ release responds to temperature change.

For the oxidation of OC_{petro} in the Laval catchment, we find a Q₁₀ value of 2.2 ± 0.5 ($R^2 = 0.33$, p-value < 0.001 , $n = 27$). This is within uncertainty of the global median Q₁₀ value of 2.4 estimated for soil respiration of recent plant-derived organic matter⁴¹, and the mean Q₁₀ of 3.0 ± 1.1 for the 0-20°C range from a global soil respiration database³⁸. It is also equivalent to the value of 2.4 ± 0.3 observed for a whole-soil warming experiment³⁷. Such high Q₁₀ values demonstrate that the OC_{petro} in these rocks, which are type III kerogen with a moderate to low thermal maturity^{25,29}, is highly reactive. These Q₁₀ values could reflect first order reaction kinetics, and hence occur abiotically. For OC_{petro} oxidation, apparent Ea is $45 \pm 11 \text{ kJ.mol}^{-1}$ ($R^2 = 0.53$, p-value < 0.001 , $n = 18$) for chamber H6. These values are lower than the lowest Ea of $\sim 100 \text{ kJ.mol}^{-1}$ determined for abiotic thermal oxidation of sedimentary organic matter⁴². The lower Ea for OC_{petro} oxidation at our site supports that microbial activity can enhance the oxidation kinetics of OC_{petro}^{42,43}, as it does for plant-derived organic matter oxidation in soils⁴⁴.

Our findings challenge existing models of how chemical weathering impacts the long-term carbon cycle. At present, chemical weathering is considered a negative feedback on climate change, with silicate weathering by carbonic acid acting as a CO₂ drawdown that increases with atmospheric CO₂ concentrations (and associated temperature and runoff)⁴⁵. The global CO₂ drawdown is estimated to be 90-120 MtC.yr⁻¹. For basalts, considered the most weatherable of silicate rocks, their sensitivity to temperature reveals an Ea of $42 \pm 3 \text{ kJ.mol}^{-1}$

(ref. ⁴⁶) and a Q_{10} of 2.0 ± 0.2 (calculated based on data in ref. ⁴⁶). However, sedimentary rocks dominate Earth's continental surface^{10,11} and global OC_{petro} oxidation¹² rates are $\sim 40\text{-}100 \text{ MtC yr}^{-1}$. This CO_2 release is likely to be dominated by weathering of shales¹², with a low to moderate thermal maturity and OC_{petro} content similar to rocks at the Draix Critical Zone Observatory, rather than rocks with higher metamorphic grades⁴⁷. Erosive landscapes like the one studied here are likely to contribute importantly to global rates of OC_{petro} oxidation^{3,17,18}. The role of temperature on oxidative weathering fluxes in locations with low denudation rate, that have deep weathering fronts^{48,49} remains to be explored.

If the Q_{10} values for OC_{petro} oxidation that we measure are found to be more widespread, for a Q_{10} value of 2 (Fig. 3) a global temperature increase of 2 to 4 °C would increase the CO_2 emissions from OC_{petro} oxidation by 15% to 30%. Such imbalances in geological CO_2 emissions are unlikely to be sustained for more than $\sim 10^6$ years (ref. ⁵⁰), and thus call for the operation of the global chemical weathering thermostat to be re-examined⁴⁵. The co-occurrence of sulfide and carbonate minerals in sedimentary rocks at the global scale, and the modern global fluxes of CO_2 release from the carbonate dissolution by sulfuric acid are less well known^{8,16}, but our Q_{10} values suggest that this could further enhance a positive feedback on atmospheric CO_2 concentrations associated with oxidative weathering. Overall, we propose that oxidative weathering of sedimentary rocks is a previously overlooked positive feedback that responds to global climate change. At present, such a temperature-controlled CO_2 release by OC_{petro} oxidation and/or CaCO_3 -dissolution by sulfuric acid has not been captured in geological carbon cycle models⁵¹. Our data suggest that they should be, and that their temperature sensitivity should be considered alongside that of silicate weathering.

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Author contribution statement: RGH conceived the research and designed the study with GS. GS and SK built and maintained the chambers. GS and RGH carried out fieldwork with additional assistance from TR, TC and MD. GS led the CO₂ flux measurements and all related calculations and analysis. SK collected and provided field temperature data, discharge and precipitation data. MHG provided materials for sampling CO₂ for isotopic analyses. GS and MHG carried out geochemical analyses. GS and RGH analysed the results. GS and RGH wrote the paper with inputs from all co-authors.

Competing interest statement: We declare no competing interest.

Figures legends/captions

Figure 1: The Laval field site. **a:** Chambers H4, H6, H7, H8 and H13 were installed, alongside the chamber for the temperature probe, in Callovo-Oxfordian marls. The operator (silhouette, ~185 cm) is measuring CO₂ flux in chamber H6 with a CO₂ analyser connected to the MS³ (molecular sieve sampling system; ref. ⁵²). **b:** View of H7 and H8 (dashed white square in a), with H7 installed in bedrock below the surface soil. **c:** The chamber design²¹ for H6, with white PVC tubing to be 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. **d:** Schematic diagram of the closed-loop MS³ connected to the chamber. Gas flow pathways (blue arrows) are controlled by opening and closing the clips (red bars) to measure CO₂ concentration (via the bypass) and scrub CO₂ (soda lime) or trap a CO₂ sample (zeolite molecular sieve).

Figure 2: The source of CO₂ sampled from chambers H4 and H6 based on its isotopic composition. Radiocarbon composition (F¹⁴C) *versus* stable carbon isotopes (δ¹³C) of the CO₂ samples from H4 and H6 (circles). End-member values were assessed from direct measurements of atmospheric CO₂ in the Laval catchment (Draix, France) (black crosses), carbonates (blue crosses) and rock organic carbon (OC_{petro}; brown crosses) contained in the Jurassic marls. The chamber CO₂ samples show a high proportion of geologic carbon (low F¹⁴C), implying only a small contribution from atmospheric CO₂. δ¹³C values are generally

closer to the carbonate endmember, showing that chamber CO₂ is mostly sourced by carbonate dissolution by sulfuric acid. Radiocarbon can be sourced from atmospheric CO₂ via carbonic acid weathering of carbonate (Reactions R6-8) and/or leaks during sample collection (Methods).

Figure 3: Measured total CO₂ emissions from rock weathering in the Laval catchment (Draix, France) for 2.5 years from late December 2016 to early May 2019. a: Total CO₂ flux (carbonate-derived and OC_{petro}-derived) measured in chambers H4 and H6 compared to the temperature measured in the rock interior (black line [daily temperature average] and grey envelope [daily amplitude]; Methods). **b:** Total CO₂ flux measured in chambers H4, H6, H7, H8, H13 normalized to their amplitude parameter (F_0) (Methods and Supplementary Table 2) compared to temperature measured in the rock interior. Error bars indicate standard deviation on the flux measurements (Methods) when larger than the symbol size.

Figure 4: Temperature sensitivity of total CO₂ release by sedimentary rock weathering. Growth exponential fits of the CO₂ flux versus temperature in the rock interior: $y = F_0 \exp(\alpha x)$. **a:** Individual fits on the data for chambers H4 and H6 (bold lines) and their 1 σ envelope (dashed lines). **b:** Fit (bold line) on all CO₂ flux measured in chambers H4, H6, H7, H8, H13 normalized to their amplitude parameter (F_0) (Methods and Supplementary Table 2) and its 1 σ envelope (dashed lines). Q_{10} thermal factor is $\exp(10\alpha)$. Statistics on each fit are available in Supplementary Table 2. Error bars indicate standard deviation on the flux measurements, when larger than the symbol size (Methods).

Figure 5: Variability in the total CO₂ emissions compared to the elevation of the rock chambers above the Laval river bed. Box plots show the full measured variability in each

chamber (H4, H6, H7, H8, and H13), the minimum value, the 25th percentile, the median, the 75th percentile, the maximum value and outliers (crosses). Dashed line (– · –) is the elevation *versus* CO₂ flux median linear fit ($r^2 = 0.98$; $p\text{-value} < 0.001$). Symbols are the amplitude parameter F_0 (Methods and Supplementary Table 2) obtained through the growth exponential fits on data for each chamber. Error bars show 1σ uncertainty on the amplitude parameter. Dashed line (- -) is the elevation *versus* amplitude parameter linear fit ($r^2 = 0.98$; $p\text{-value} < 0.001$). See Supplementary Tables 2 and 4 for numerical values.

Methods

Field area. The Laval catchment (Draix, France) in the Draix-Bléone observatory is located in the French southern Alps, part of OZCAR the French network of observatories for the study of the critical zone²³. The Laval catchment (0.86 km²; altitude between 800 and 1250 m) is a headwater catchment that has been instrumented since 1982 to monitor rainfall, water discharge, suspended load and bedload transport^{22,53,54}. Meteorological data including air temperature and humidity are also continuously recorded^{53,54}.

The Laval catchment is composed of finely bedded, mechanically weak and erodible Jurassic black marls (Bathonian, Callovian and lower Oxfordian ages). From 1985 to 2016, mean annual rainfall was 916 ± 175 mm. The catchment is characterized by a Mediterranean climate with a hot and dry summer. During summer, rain events occur during abrupt, short and intense thunderstorms. Spring and autumn are characterized by rain of lower intensity but lasting up to several days. It is also a mountain climate with freeze-thaw cycles during wintertime. The combination of freeze-thaw and wet-dry cycles are important in the physical weathering of marls^{22,54}, and combined with the intense precipitation, incised channels and steep hillslopes, leads to high erosion rates of 7 to 10 mm/yr (ref. ^{21,22,25}).

These conditions limit the development of soils but favour the development of a dense gully network typical of badlands. The catchment is sparsely vegetated with marls outcropping as bare rock over 68% of the catchment surface area (0.58 km²) (refs. ^{22,24}). It is thus easy to

find regolith and rocks that are devoid of soils and roots (Fig. 1a). Bare rock outcrops are characterized by partly weathered marls and regolith. Regolith is generally ~20 cm deep: the upper ~3 cm is a loose detrital cover composed of cm-sized fragments of marls; from ~3 to 10 cm is the loosened somewhat fragmented upper regolith; from ~10 to ~20 cm is the compact lower regolith; below is the unweathered marl bedrock^{22,26}. Lateral variation in the regolith thickness is usually observed with larger thickness on crests, intermediate in gullies and minimal in talwegs²⁶.

In situ rock weathering chambers. The experimental setup has been detailed previously²¹. Here in summary, each chamber is drilled directly into the rock with a rock drill. The rock face is cleared before drilling. Rock powder left inside the chamber after drilling is blown away with a pressurized air gun. The entrance of the chamber is fitted with a ~3cm-long PVC tube, in which a rubber stopper is inserted. Two glass tubes are inserted through the rubber stopper (Fig. 1). The external parts of the glass tubes that stick out of the stopper are fitted with Tygon® tubing. In order to isolate the chamber from the atmosphere, the Tygon® tubing is clipped, and silicon sealant is placed around the entrance of the chamber. The inside wall of the chamber is the exchange surface area between the rock pore space and chamber headspace, and through which the rock CO₂ emission passes. We designed the chamber dimensions (40 cm deep and 3 cm diameter) so that the ratio surface/volume is large, benefitting CO₂ flux measurements. Chambers are stable, required little maintenance, and stayed in the field for the entire experiment making it possible to monitor CO₂ emissions over seasonal cycles.

Five chambers were installed in barren marls on the left side of the Laval river (N44.1406, E06.3628) within a distance of 12 metres on the North-facing side of the Laval stream valley (Figure 1a). Chamber H7 is located 1.27 m above the river bed and 0.46 m above

chamber H8. Seven metres upstream, chamber H13 was installed at an elevation 1.90 m above the river bed. Another five metres upstream, chamber H6 was installed at an elevation of 2.31 m above the river bed, and 0.98 m above chamber H4.

In this study, we present data from a set of 5 chambers that had the same aspect; were on the same rock outcrop; had no roots present; remained well sealed; and were not destroyed quickly by flooding or wild animals. Other chambers were drilled that were not included here because they were either: test chambers from a reconnaissance field trip (H1-3); had a poor seal (H5); as a dummy chamber for a temperature probe (H12); drilled on a south facing slope partly in colluvium (H9-11 and H14). After the ~2.5-year long experiment, all chamber materials were removed from the field site.

Flux measurements. Flux measurements and calculations were described previously in ref. ²¹. In summary, to measure the CO₂ flux, the chamber is connected to an infra-red gas analyser (EGM 5 Portable CO₂ Gas Analyzer, PP Systems, USA) using the molecular sieve sampling system (MS³) described in ref. ⁵². This allows the operator to first bring the chamber CO₂ concentration to ~400 ppm of the local atmosphere (using soda lime or a zeolite material to remove CO₂ from the chamber), before then recording the CO₂ accumulation in the chamber over time. During each field visit, we typically recorded a sequence of n repeats of 5-minute-long accumulations of CO₂ for each chamber. The number of repeats (n) was at least 7 but usually 8 or more. From one sequence, we calculated n rates (q_i) of CO₂ accumulation ($\mu\text{gC}\cdot\text{min}^{-1}$) fitting the data with the exponential model described in ref. ⁵⁵ over a fitting window of 3.5 minutes after CO₂ concentration typically reaches ~400 ppm in the chamber. The first 3 measurements of CO₂ accumulation are used to purge the CO₂ that accumulated in the rock pore space around the chamber during the hours before measurements. Hence, the first 3 calculated rates were excluded, and we calculated an average CO₂ accumulation rate for the chamber:

$$\bar{q} = \frac{1}{n-3} \sum_{i=4}^n q_i \quad (3)$$

We take this value as representative of the rate at which CO₂ evades from the naturally fractured, porous rock mass at the time of the sequence of the repeated measurements. The uncertainty on the average rate was taken as the standard deviation of the $n-3$ considered individual rates. From these series we also calculated a scaling factor (A) for each sequence:

$$A = \bar{q}/q_1 \quad (4)$$

For each chamber, over 2.5 years we obtained an averaged factor $\bar{A}$ and its standard deviation. For some of the measurement sequences we did not manage to measure a full series of at least 7 repeats. In this case the CO₂ flux was obtained by scaling the very first repeat using parameter $\bar{A}$. In that case, the average $\bar{q}$ was calculated as follows:

$$\bar{q} = q_1 \times \bar{A} \quad (5)$$

Standard deviation of $\bar{A}$ was propagated to provide an uncertainty on the scaled rate. Finally, we converted each obtained CO₂ accumulation rate $\bar{q}$ (μgC.min⁻¹) into a CO₂ flux (F) (mgC.m⁻².day⁻¹) using the internal surface area (S) of the considered chamber:

$$F = 1440 \bar{q}/S \quad (6)$$

To test whether our approach (chambers drilled in the rock) yields comparable CO₂ fluxes to more traditional surface chambers, we installed two short-term surface chambers in October 2017. The chambers were plastic boxes (length = 19.5 cm, width = 8.2 cm and height = 3.5 cm) which were sealed to the rock face with silicone sealant two days before measurements were made. These were located on the same outcrop as the drilled rock chambers, at a similar elevation above the river channel to chamber H8. The measured fluxes on 12/10/2017 (determined in the same way as our rock-chambers, with pCO₂ lowered to ambient atmosphere, and then left to build up) were 138 ± 14 mgC m⁻² day⁻¹ for surface chamber W01, and 241 ± 13 mgC m⁻² day⁻¹ for surface chamber B02. During the same sampling trip (with a temperature

of between 10 and 11°C in the rock during measurement), these fluxes are consistent with those measured for Chamber H8 ($191 \pm 39 \text{ mgC m}^{-2} \text{ day}^{-1}$) at a similar relative elevation above the river channel, and slightly lower than that measured for Chamber H7 ($323 \pm 85 \text{ mgC m}^{-2} \text{ day}^{-1}$) which is located at a higher elevation. These are small offsets in the context of the environmental controls on the flux that change the flux by a factor of 2 over 10 degrees. Therefore, our method yields results comparable to more traditional surface chambers. The advantage of the rock chambers is their: i) large surface area to volume ratio, meaning CO₂ could be trapped more efficiently for isotopic analysis; ii) longevity, allowing us to revisit the same substrate at each field visit.

CO₂ isotopic composition. After measuring the CO₂ accumulation in the chamber, the MS³ enables the operator to trap the CO₂ gas in zeolite molecular sieves (type 13X) (ref. ^{21,52}). The CO₂ samples trapped from the chambers were extracted from the zeolite molecular sieve in the laboratory by heating. Extracted CO₂ is then purified cryogenically under vacuum⁵⁶. An aliquot of the CO₂ sample is used to measure its stable carbon isotopic composition ($\delta^{13}\text{C}$) by Isotopic Ratio Mass Spectrometry (Thermo Fisher Delta V; results expressed relative to the Vienna Pee Dee Belemnite (VPDB) standard). A further aliquot was graphitized to measure its radiocarbon (^{14}C) concentration by Accelerator Mass Spectrometry at the Scottish Universities Environmental Research Centre (SUERC). Following convention, ^{14}C measurements were corrected for isotopic fractionation using the measured sample IRMS $\delta^{13}\text{C}$ values, and reported in the form of the fraction modern, i.e., the $F^{14}\text{C}$ notation⁵⁷.

We collected atmospheric CO₂ samples using the MS³ coupled to the CO₂ gas analyser by circulating atmospheric air through the zeolite. Atmospheric CO₂ was extracted and analysed for its isotopic composition as described above.

Carbon isotope composition and contents of the rock. After having drilled the chamber, we sampled the powdered rock for inorganic and organic carbon analysis. Samples were freeze-dried and crushed to fine powder. Total carbon (TC) and Inorganic carbon (IC) content of the rock samples were obtained using an elemental analyser (Jena Multi EA 4000). Rock organic carbon content was obtained by difference ($OC_{\text{petro}} = TC - IC$). Carbon contents are reported in % weight. Stable carbon isotope composition of the rock organic carbon (OC_{petro}) was obtained using a Costech Elemental Analyser coupled to a Thermo Delta V Isotope Ratio Mass Spectrometer (IRMS) run with normalising standards (international and internal) and external standards to check precision and accuracy. Stable carbon isotope of the rock inorganic carbon was obtained using a carbonate dissolution device (Thermo Gas Bench II) coupled to an IRMS (ThermoScientific MAT 253). Stable carbon isotopes ($\delta^{13}C$) are reported in ‰ compared to the VPDB standard.

Mixing model for source of CO_2 . We assume that the isotopic composition of the trapped CO_2 reflects a three-component mixture of carbon:

$$\begin{bmatrix} 1 & 1 & 1 \\ \delta^{13}C_{OC} & \delta^{13}C_{SA} & \delta^{13}C_{CA} \\ F^{14}C_{OC} & F^{14}C_{SA} & F^{14}C_{CA} \end{bmatrix} \cdot \begin{bmatrix} f_{OC} \\ f_{SA} \\ f_{CA} \end{bmatrix} = \begin{bmatrix} 1 \\ \delta^{13}C_{Ch} \\ F^{14}C_{Ch} \end{bmatrix} \quad (7)$$

where f is the mass fraction of CO_2 sourced by the oxidation of the rock organic carbon (f_{OC} ; Reaction R1), the dissolution of carbonate minerals by sulfuric acid (f_{SA} ; Reactions R2-3), and the dissolution of carbonate minerals by carbonic acid coupled to sulfuric-acid-driven degassing (f_{CA} ; Reactions R6-8)). Subscript “Ch” stands for the CO_2 sampled from the chambers. The terms $\delta^{13}C$ and $F^{14}C$ stand for the stable carbon isotope and radiocarbon compositions of the three possible sources of CO_2 listed above and of the CO_2 sampled in the chamber.

The $\delta^{13}\text{C}$ and $F^{14}\text{C}$ values are based on the chemical reactions (Eq. (1), (3) and (6-8)), on the fractionation factor Δ between bicarbonate and CO_2 (ref. ⁵⁸), and on measurements of OC_{petro} , CaCO_3 , and atmospheric CO_2 sampled from the field site (Supplementary Information). The $F^{14}\text{C}$ of CaCO_3 and OC_{petro} are assumed to be 0 (ref. ²¹). For the oxidation of rock organic carbon, Reaction (R1) yields:

$$\delta^{13}\text{C}_{\text{OC}} = \delta^{13}\text{C}_{\text{OC}_{\text{petro}}} \quad (8)$$

$$F^{14}\text{C}_{\text{OC}} = F^{14}\text{C}_{\text{OC}_{\text{petro}}} = 0 \quad (9)$$

For the dissolution of carbonate minerals by sulfuric acid, Reaction (R3) yields:

$$\delta^{13}\text{C}_{\text{SA}} = \delta^{13}\text{C}_{\text{CaCO}_3} \quad (10)$$

$$F^{14}\text{C}_{\text{SA}} = F^{14}\text{C}_{\text{CaCO}_3} = 0 \quad (11)$$

For the dissolution of carbonate minerals by carbonic acid coupled to CO_2 degassing driven by sulfuric acid, Reactions (R6-8) yields:

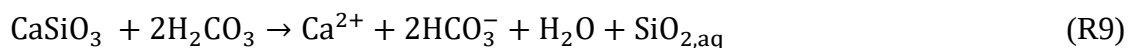
$$\delta^{13}\text{C}_{\text{CA}} = \frac{1}{2}(\delta^{13}\text{C}_{\text{atm}} + \Delta + \delta^{13}\text{C}_{\text{CaCO}_3}) - \Delta \quad (12)$$

$$F^{14}\text{C}_{\text{CA}} = \frac{1}{2}(F^{14}\text{C}_{\text{atm}} + F^{14}\text{C}_{\text{CaCO}_3}) = \frac{1}{2}F^{14}\text{C}_{\text{atm}} \quad (13)$$

Errors on the results were calculated based on a Monte-Carlo simulation of error propagation using the standard deviation of the measured $\delta^{13}\text{C}$ and $F^{14}\text{C}$ of the end-members and CO_2 sampled in the chambers.

The mixing approach assumes that the ^{14}C -enrichment comes from atmospheric CO_2 dissolved in rain, which is consistent with the higher $F^{14}\text{C}$ values of the CO_2 sampled from chamber H4 located close to the water table, compared to the CO_2 with lower $F^{14}\text{C}$ values sampled from chamber H6 located away from the water table (Fig. 2 and 5) .

Alternatively, the ^{14}C enrichment may occur through the weathering of silicate minerals by carbonic acid coupled to the degassing of CO_2 driven by sulfuric acid (Reaction R8):



However, as the kinetics of dissolution of silicate minerals are slower than those of carbonate⁵⁹, in rapidly eroding settings, this pathway is likely to be of second order importance compared to the dissolution of carbonates. This is corroborated by the chemistry of the Laval river waters yielding very low bicarbonate-to-sulfate ratio (0.35; ref. ^{24,60}) compatible with that of 0 resulting from the two carbonate dissolution pathways Reaction (R3) and (R7-8).

Natural leaks around the chamber entrance, or within the gas sampling case^{21,52} could also explain the ¹⁴C enrichment of the sampled CO₂. However, the pCO₂ in the chambers was always higher, sometimes by thousands of part per million, than that of the atmosphere. Thus, the CO₂ must diffuse out of the rock face towards the atmosphere, and atmospheric contamination from leaks around the chamber entrance should be minor.

Activation energy (Ea). Arrhenius equation relates the rate of a reaction k (here a CO₂ flux) to the absolute temperature (T in Kelvin), gas constant (R), a pre-exponential factor A and the activation energy of the reaction (Ea):

$$k = Ae^{\frac{-Ea}{RT}} \quad (9)$$

Rearranging the logarithm of equation (14) yields:

$$-R \times \ln(k) = -R \times \ln(A) + Ea/T \quad (15)$$

Equation (15) has the form of a linear equation ($y = b + mx$) where y is $-R \times \ln(k)$ and x is $1/T$, with the slope m being the activation energy (Ea). Thus, linear fitting $-R \times \ln(k)$ as a function of $1/T$ returns Ea.

Environmental data. Since 2000, the air temperature is recorded every 10 minutes using a HMP45C temperature and relative humidity probe (Campbell Scientific Inc.) at the “Le Plateau” automated weather station. The weather station is located at the outlet of the Laval

catchment, at the same elevation and 200 metres from the field area where headspace chambers were installed.

In order to estimate the temperature inside the chambers, we drilled a chamber on the same outcrop (Fig. 1). On 12/10/2017, this chamber was equipped with a PT100 temperature sensor (Campbell Scientific Inc.) coupled to a CR1000 control datalogger (Campbell Scientific Inc.). The temperature sensor was inserted into the chamber through the rubber stopper. Then we sealed the chamber to insulate it from the exterior. Temperature was recorded every 5 minutes. We considered this temperature record as representative of the rock temperature for all the chambers located on the same outcrop (H4, H6, H13, H7 and H8). We could not record chamber temperature for almost 10 months from 14/12/2016 to 11/10/2017, a period that includes the four first field trips. Instead we reconstructed the chamber temperature from the “Le Plateau” air temperature using a calibration curve. The calibration is based on a 12-month period of overlap between temperature recorded in the chamber and the air temperature recorded at the “Le Plateau” weather station, from 13/10/2017 and 24/10/2018. Over this period, we return a significant correlation (Fourier model; $R^2 = 0.97$; $p\text{-value} < 0.001$; $n = 377$; Extended Data Fig. 5-6) between the daily average temperature measured on day “d” in the chamber ($T_{\text{chamber}, d}$) and factor γ , which we defined as the air temperature averaged over a 3-days window preceding day “d”, and weighed by the fractional duration of daylight (L) at the Laval catchment latitude:

$$\gamma = \frac{1}{3} \sum_{i=d-3}^{d-1} [T_{\text{air}, i} \times L_i] \quad (16)$$

Weighting the air temperature by the fractional duration of daylight approximately accounts for the duration of exposure of the outcrop to daylight.

At the outlet of the Laval catchment, the river water discharge is continuously recorded at a gauging station equipped with a calibrated flume (Parshall flume) and two level recorders (ultrasonic sensor and numerical rule) (ref. ⁵⁴).

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Data availability

All data that support the findings of this study are available from the Natural Environment Research Council (NERC) – British Geological Survey (BGS) National Geoscience Data Centre with the identifier <https://doi.org/10.5285/efc082aa-5c2b-4afb-aec8-344aebaea653>

Code availability

Custom Matlab® codes and accompanying pCO₂ source data are available on request from the corresponding authors.

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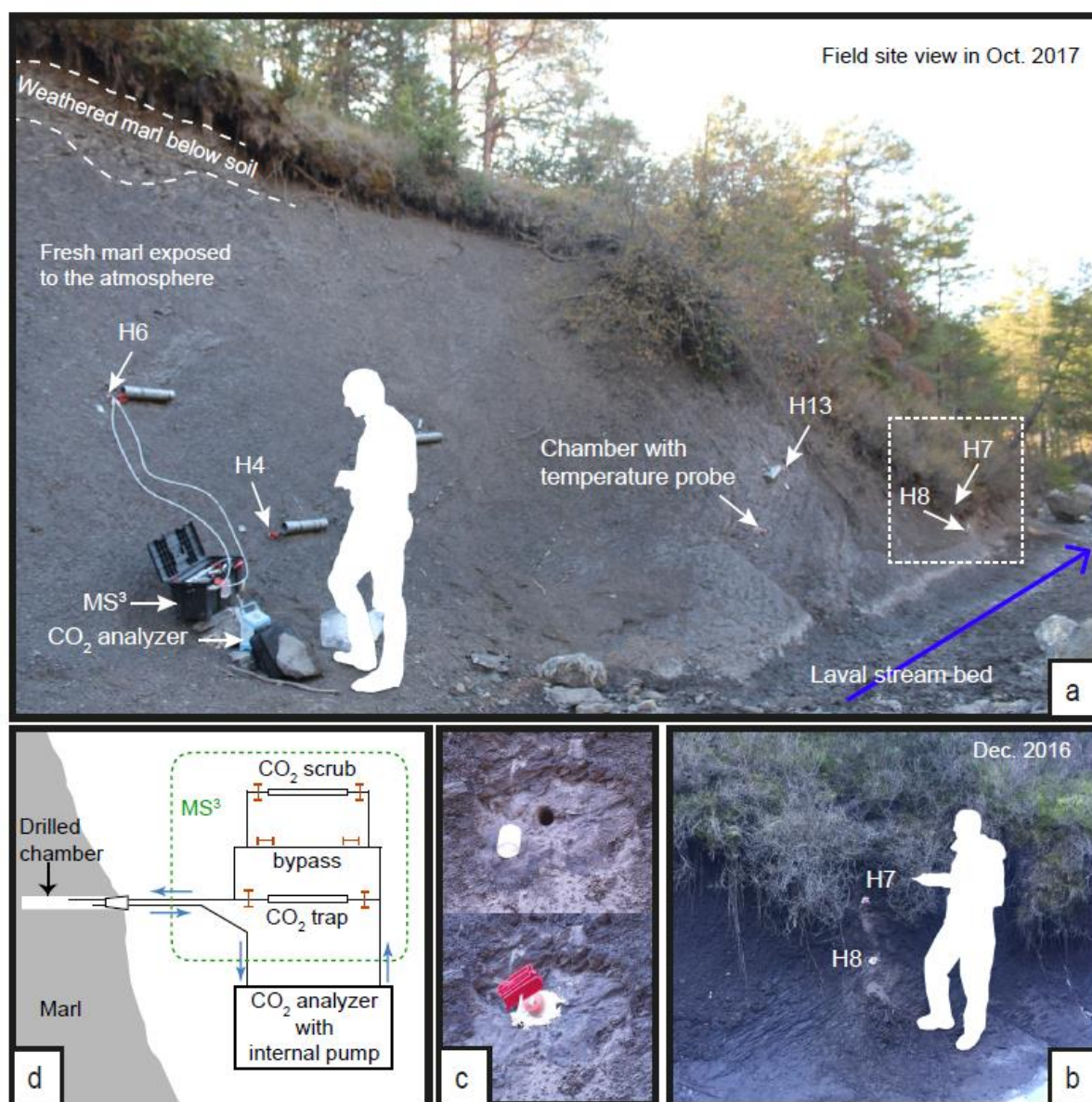


Figure 1

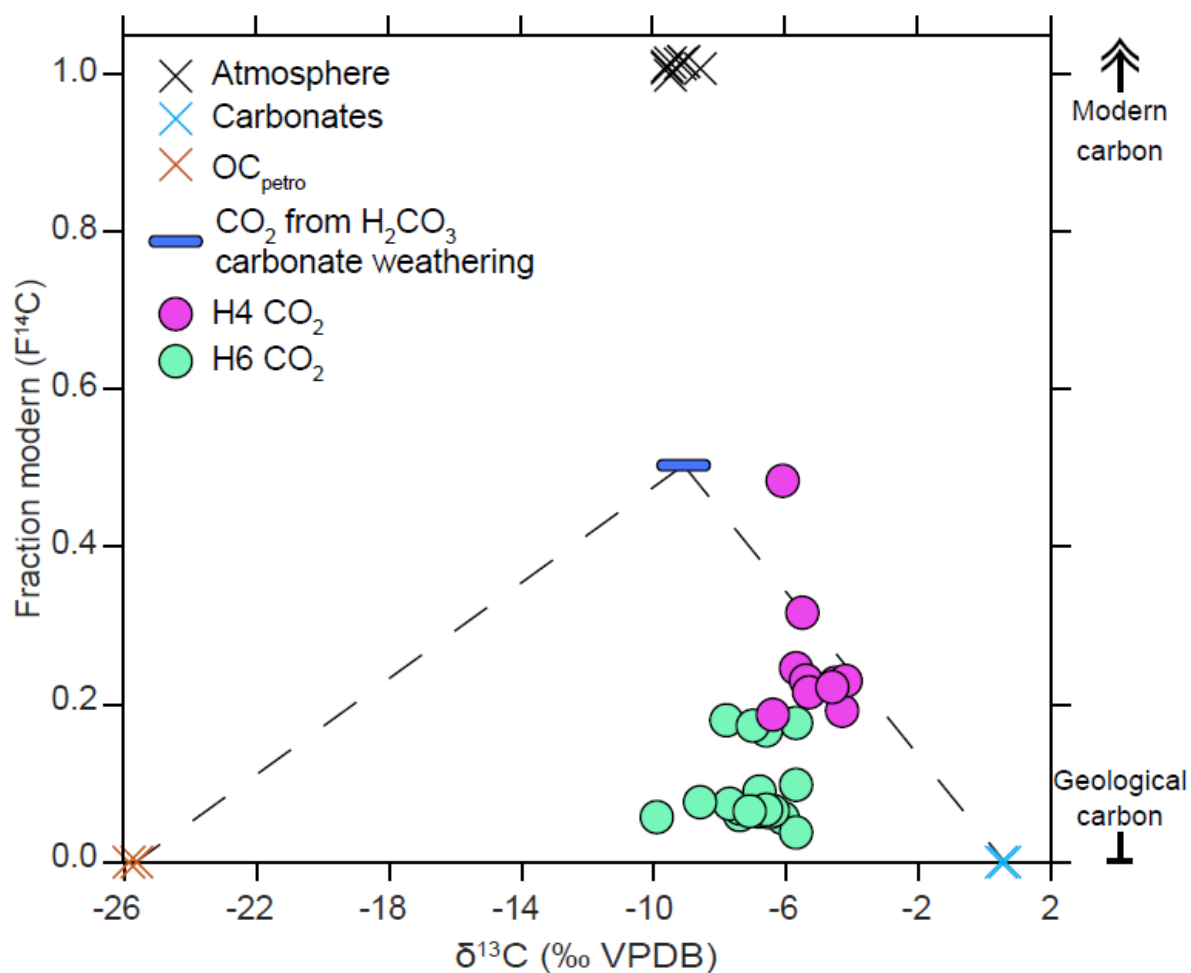
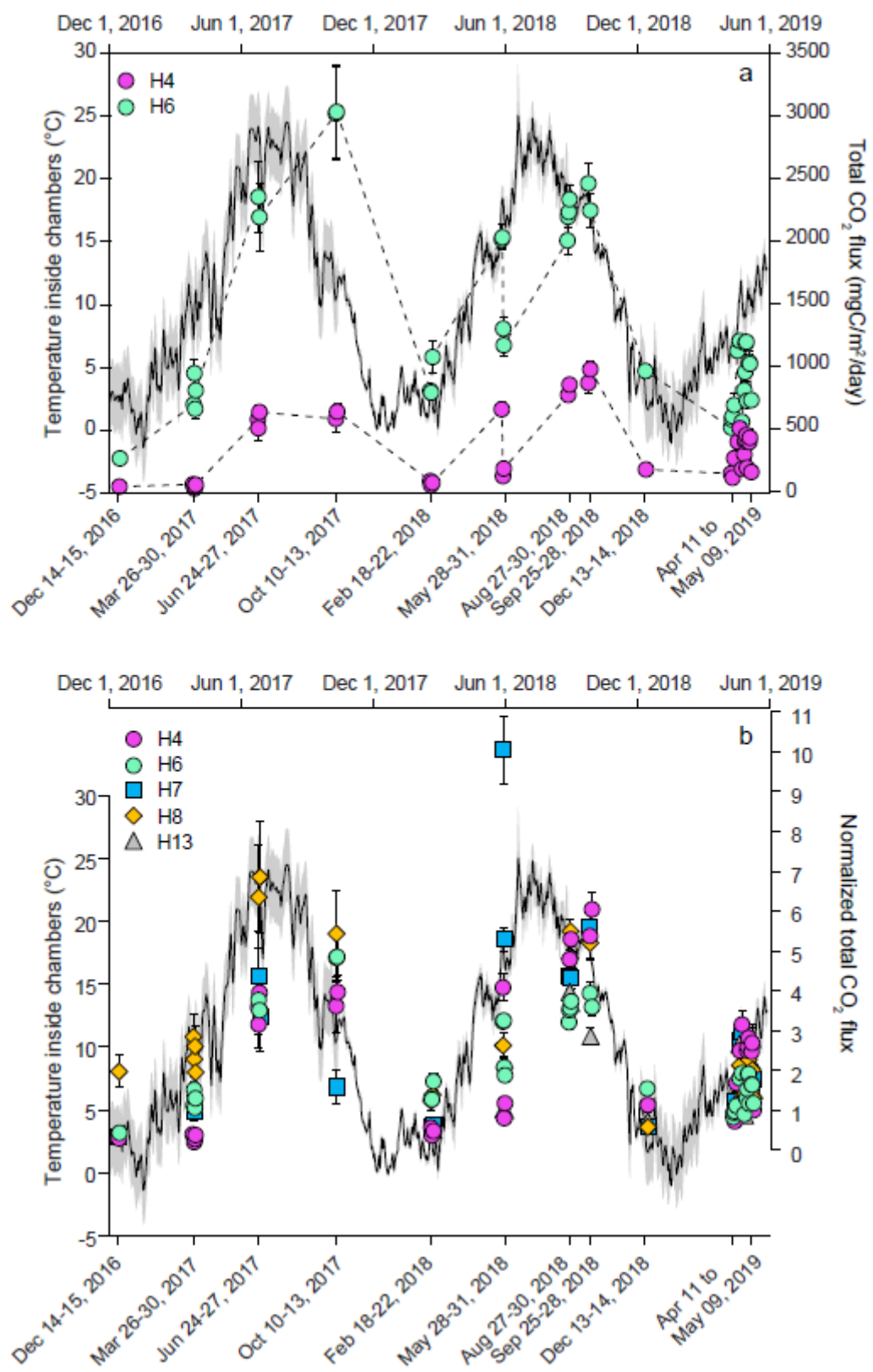


Figure 2

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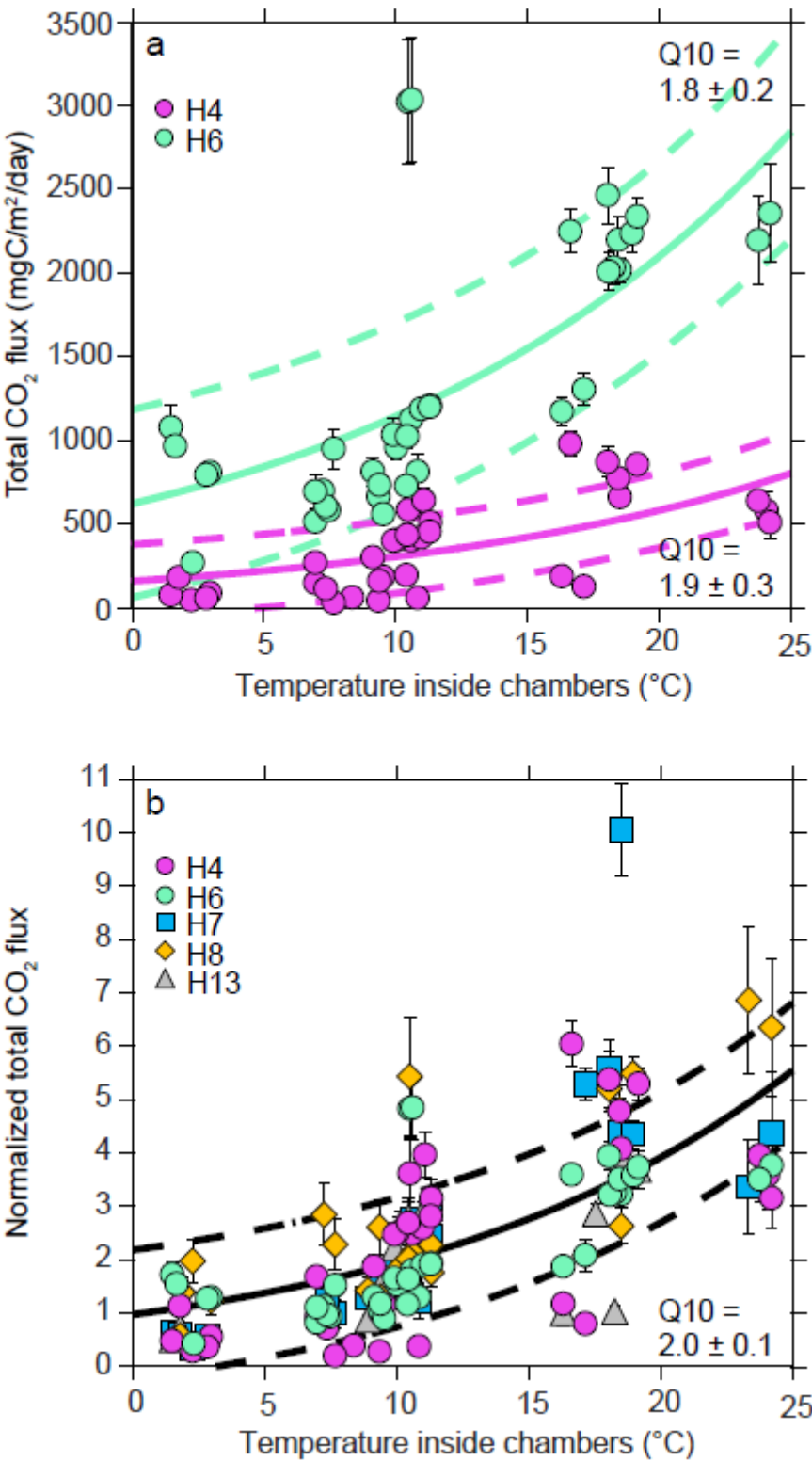
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Figure 3

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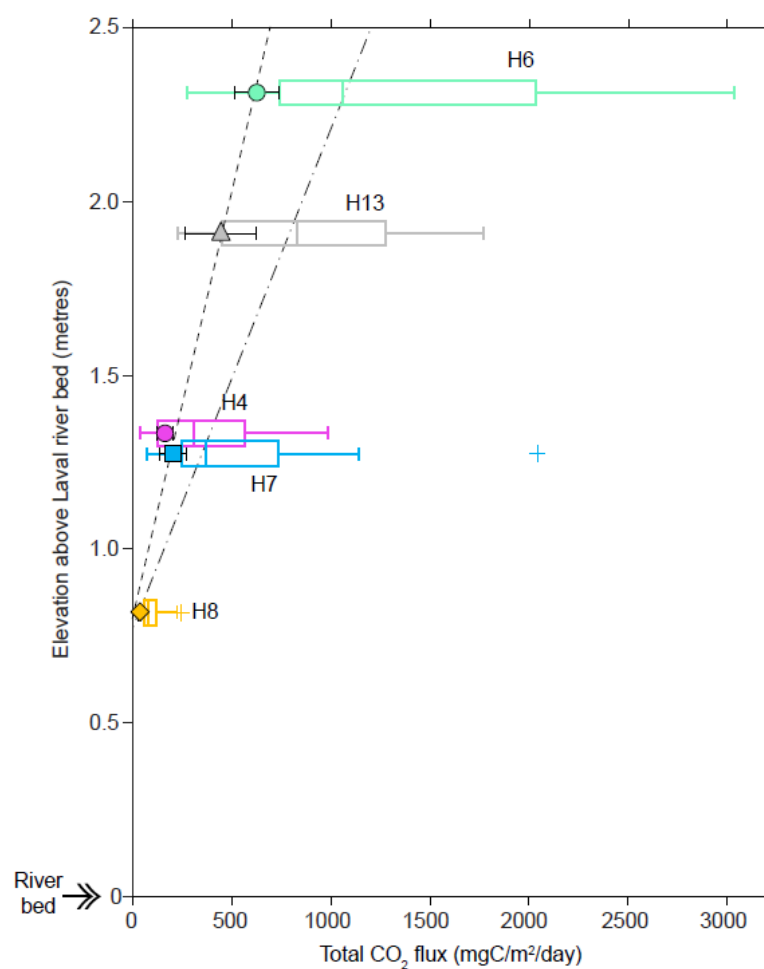
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Figure 4

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807 **Figure 5**

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819 **Extended Data**

820 **Extended Data Figures and Captions**

821 **Extended Data Figure 1:** CO₂ emissions measured in the Laval catchment (Draix, France)

822 (red square; Supplementary Table 4) compared to respiration CO₂ flux in various soil types

823 (black hyphens). Median values are shown with the symbols, the minimum-maximum range is

824 indicated with solid lines. As maximum value for cropland exceeds the scale of the y-axis,

825 upper part of the cropland range is dashed and maximum value is indicated. The respiration

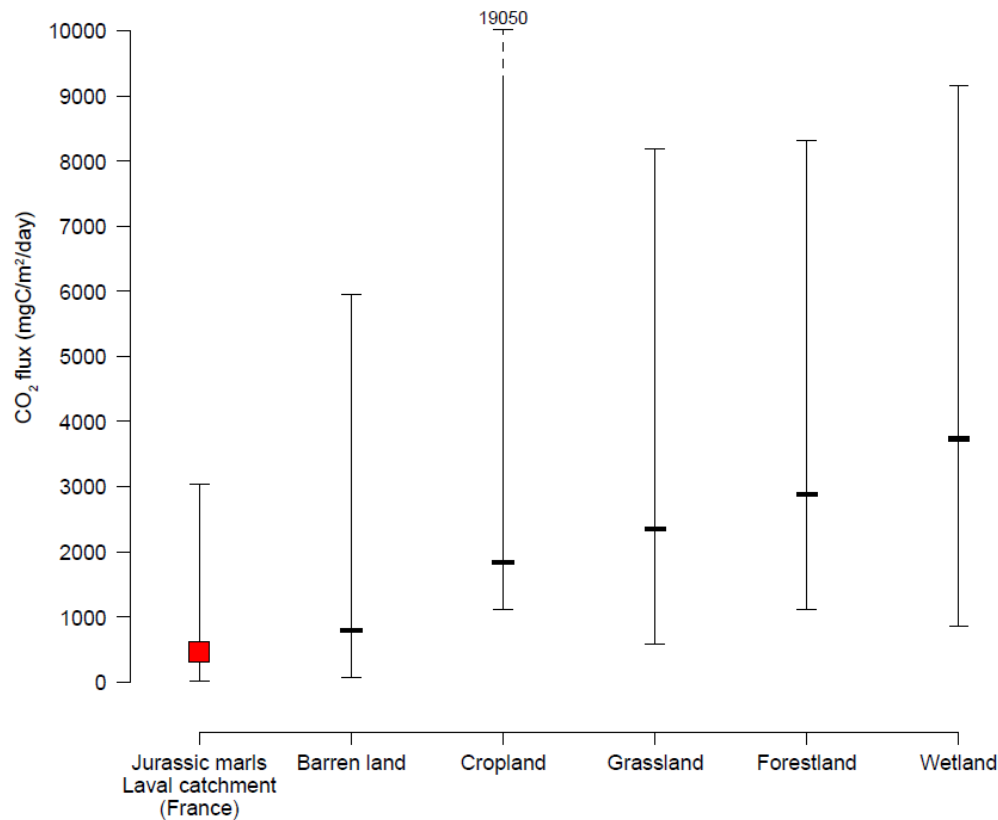
826 soil compilation is from ref. ³⁰. Note that the CO₂ emission from oxidative weathering of

827 sedimentary rocks in the Laval catchment reaches the magnitude of the CO₂ emissions from

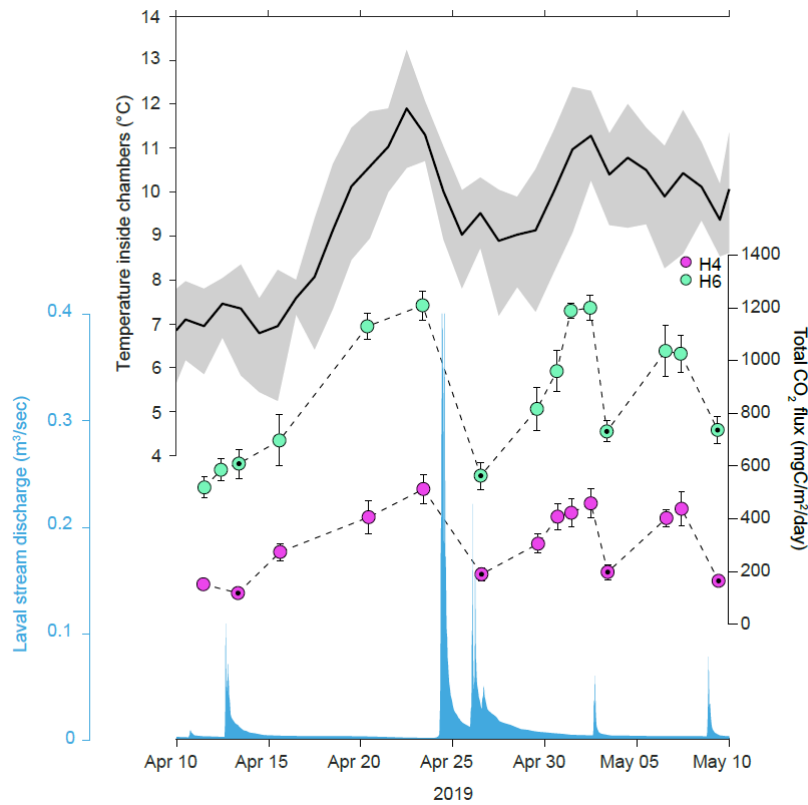
828 respiration of all type of soils.

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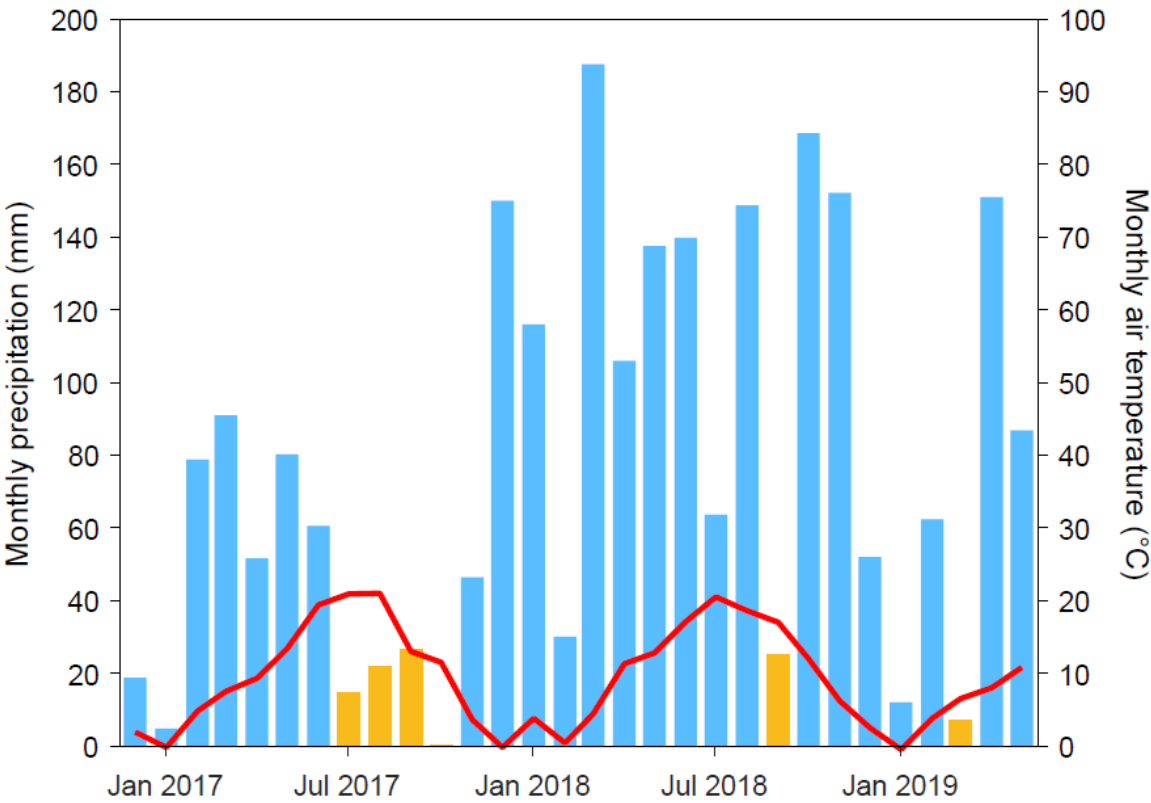
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Extended Data Figure 2: Temperature and hydrological controls on total CO₂ emissions recorded in chambers H4 and H6 for one month from 10/04/2019 to 10/05/2019. Upper panel: Daily temperature average (black line) and amplitude (grey envelope) in the rock interior. Lower panels: CO₂ flux measured in chamber H4 (pink circles) and H6 (green circles). Error bars indicate standard deviation on the flux measurements (Methods) when larger than the symbol size. Circles with a black dot inside denotes CO₂ flux measurements performed in average 17 hours (15 to 19 hours) after a rainfall event. The rain events are visible as sharp peaks in the water discharge recorded in the Laval catchment (blue envelope).



Extended Data Figure 3: Climate of the Laval catchment (Draix, France) for two and a half years from December 2016 to May 2019 (study period). Monthly rain precipitation (bars) is compared to the monthly temperature average (red line). Drought periods are represented by the orange bars. Rainfall monitoring in the Laval catchment started in 1982 (ref. 13,23). 2017 was the driest year ever recorded in the Laval catchment (annual precipitation 627 mm), whereas 2018 was the wettest (1327 mm), and 2019 the second wettest (1263 mm). Note the 4 month-long drought from July to October 2017. The climatic diagram shows the highly seasonal pattern of the air temperature in the Laval catchment.



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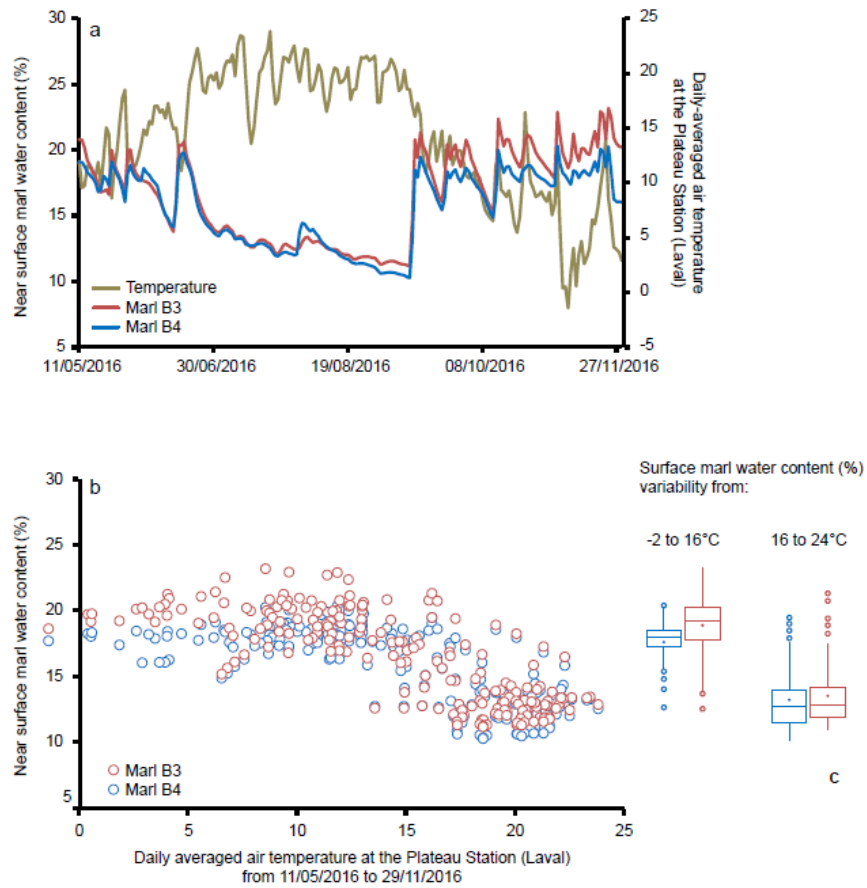
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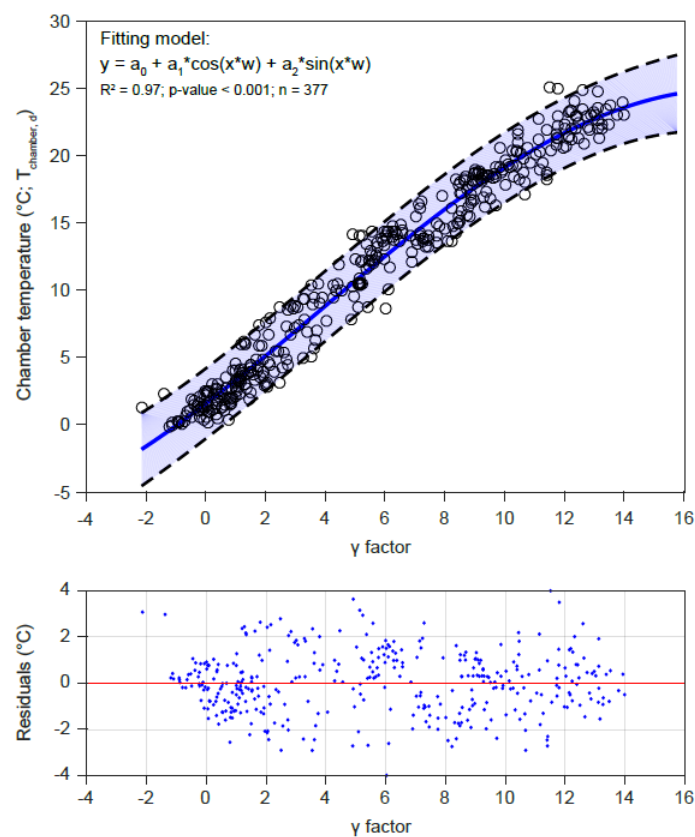
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862 **Extended Data Figure 4: a.** The near surface water content of the Laval catchment marls at
863 station B3 (red line) and B4 (blue line) and the daily-averaged air temperature (green line) at
864 “Le Plateau” weather station (located ~500 metres from station B3 and B4) from 11/05/2016
865 to 29/11/2016 (ref. ³⁶). **b.** The near surface water content at station B3 (red circles) and B4
866 (blue circles) versus daily-averaged air temperature recorded at the “le Plateau” weather
867 station. **c.** Box plots showing the variability of the near surface water content of the marls at
868 station B3 (red) and B4 (blue) for the air temperature range -2 to 16°C and 16 to 24°C. Box
869 plots show maximum, 25% percentile, median, 75% percentile and minimum values, as well
870 as the mean (dot) and outliers (circles).



Extended Data Figure 5: Calibration between the daily averaged temperature measured in the rock chamber (y-axis) and the γ factor (x-axis). The calibration aims to reconstruct the temperature in the chamber (when we could not measure it) based on the air temperature (T_{air}) measured at the “Le Plateau” weather station (located 200 metres from the field site) and the fractional daylight duration (L) at the Laval catchment latitude. Note that the γ factor is a simple function of T_{air} and L: $\gamma = f(T_{\text{air}}, L)$. For further details see Methods (section Environmental data). Upper panel: circles are calibration data obtained over a 12-month period of overlap between measured chamber and air temperature. Blue line and its envelope are the best fit and the 95% confidence interval. Lower panel: Blue dots are the residuals between the chamber temperature and the fitted model. Red line is the zero line.



Extended Data Figure 6: Measured and reconstructed chamber temperatures. Blue line is the daily averaged temperature measured in the chamber. Light blue envelope is the daily amplitude between the minimal and maximal temperatures recorded daily. Dark grey line is the reconstructed temperature in the chamber (see Extended Data Figure 4 for the calibration). The light grey envelope is the 95% confidence interval. On the lower x-axis are shown the field work campaigns.

