Measuring CO_2 Efflux From Sedimentary Rocks

The concentration of carbon dioxide (CO_2) in the atmosphere controls Earth's climate. Sedimentary rocks act as a giant geologic reservoir of carbon that can exchange CO_2 with the atmosphere. Carbon in rocks is stored in the form of organic matter (e.g. ancient plant remains) and carbonate minerals (e.g., calcite or $CaCO_3$). Erosion can act to expose sedimentary rocks to oxygen in the atmosphere, and this can lead to weathering and: i) oxidation of the sedimentary organic matter that produces CO_2; ii) oxidation of sulfide minerals (e.g., pyrite) that produces sulfuric acid which ultimately dissolves carbonate minerals and produces CO_2. In other words, when sedimentary rocks are exposed to the atmosphere, they can release CO_2 that has been locked away for millions of years. We know that this process is slow compared to human emissions of CO_2 from burning fossil fuels. However, it is likely to be a major player in the natural carbon cycle, and influences atmospheric CO_2 over thousands to millions of years.

Figure 1A. EGM-5 Portable CO_2 Gas Analyzer connected to a chamber drilled in the rock face [2], through the MS³ monitoring-sampling system [3], while we measure CO_2 efflux from sedimentary rock in the Laval stream catchment, Draix, France. *(© R. Hilton)*

Figure 1B. Equipment setup in the Waiapu River catchment, New Zealand. *(© R. Hilton)*

Figure 2. An example of the new method (EGM-5 Portable CO_2 Gas Analyzer connected to a chamber drilled in the rock face [2], through the MS^3 monitoring-sampling system [3]) being used in the Waiapu River catchment, New Zealand. *(© R. Hilton)*

Despite this recognition, this CO_2 efflux is not well constrained, mainly due to a lack of measurements of how fast this occurs and how the flux varies in space and time. The CO_2 efflux from the weathering of sedimentary rocks is generally estimated indirectly – for instance by measuring the products of reactions found dissolved in river water [1]. Until now, no direct measurements of this CO_2 efflux exist.

In order to measure the sedimentary rock CO_2 efflux in situ, Robert G. Hilton and Guillaume Soulet (Department of Geography, Durham University, UK) and Mark H. Garnett (Natural Environment Research Council, NERC, Radiocarbon Facility, East Kilbride, UK) have designed a new approach. The research is funded by the **ROC-CO_2 project funded by a European Research Council Starting Grant** (https://roc-co2.weebly.com/) and supported by the OZCAR-RI Draix-Bléone Observatory in France (https://oredraixbleone.irstea.fr/en/). The team has designed a chamber method [2] coupled to the molecular sieve sampling system (MS^3) designed in ref. [3] and using the **EGM-5 Portable CO_2 Gas Analyzer** from PP Systems. The chamber is drilled directly into the rock face that is undergoing weathering, and sealed using PVC tube, rubber bung and a series of glass tubes and Tygon® tubing. This enables the operators to connect the chamber to the CO_2 sampling system (MS^3) through the EGM-5 Portable CO_2 Gas Analyzer (*Figures 1A, 1B & 2*). The chamber dimensions, typically 40 cm deep and 3 cm in diameter, were designed so that the chamber internal area to volume ratio is high, benefiting CO_2 flux measurements.

Chambers are stable and can stay in field for several months or years making it possible to monitor possible changes in the CO_2 efflux over seasonal cycles. The design takes advantage of the MS^3 system [3] that enables the operator to trap the CO_2 actively through molecular zeolite sieves while measuring the CO_2 flux. This is a key development, as the combination of radiocarbon (^{14}C) and the stable carbon (^{12}C and ^{13}C) isotopic composition of the sampled CO_2 are needed to partition the measured CO_2 flux into its two components: the CO_2 flux from sedimentary organic matter oxidation and the CO_2 flux from the carbonate dissolution by sulfuric acid [2].

Here an example is shown of a chamber and EGM-5 in use on March 27th 2017, when a series of CO_2 flux measurements were performed while trapping CO_2 (*Figure 3A*) for isotopic measurements back in the lab. Resulting CO_2 fluxes were high (~730 mgC/m²/day) (*Figure 3B-C*). Isotopic measurements made later showed that 75% of this flux originated from the dissolution of carbonate by sulfuric acid, and that the remaining 25% was from the rock organic matter oxidation [2]. Based on this new method, Robert Hilton, Guillaume Soulet, and the ROC-CO_2 team are deploying these chambers in other locations with different rock types, while also monitoring the CO_2 flux regularly through the year to assess the temporal variability of CO_2 fluxes to be determined. Together, these data will help to improve our understanding of how the oxidative weathering of rocks impacts the carbon cycle in the geological past, the present and into the future.

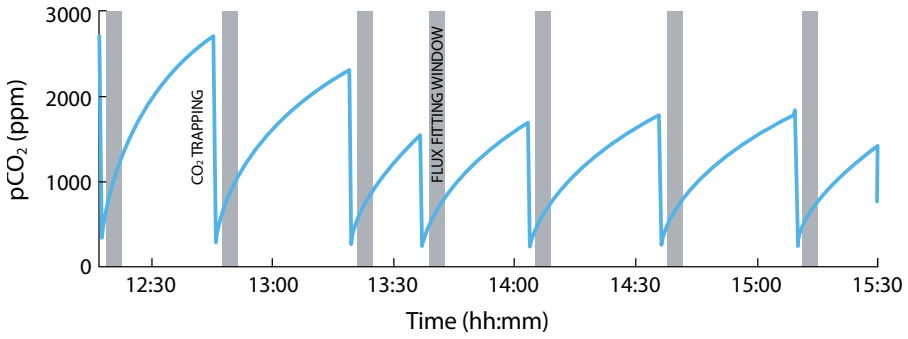

Figure 3A.

pCO_2 trace acquired using the EGM-5 Portable CO_2 Gas Analyzer from PP Systems and the CO_2 monitoring-sampling system [3] over a ~3 hour-time period. The pCO_2 increases occur when CO_2 is building up in the rock chamber, whereas the sharp pCO_2 decreases are when the CO_2 is trapped from the rock chamber into a zeolite sampler [2]. Grey area show the fitting window to calculate the CO_2 flux from the raw pCO_2 trace (please see further details in ref. [2]).

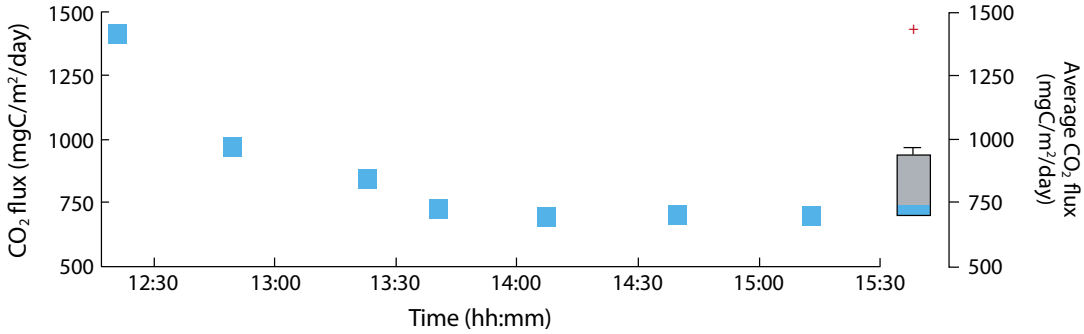

Figure 3B-C.

Calculated fluxes over the monitoring period. CO_2 flux estimates were relatively high with an average of ~730 mgC/m²/day.

References :

[1] Hilton, RG, et al., (2014) Geological respiration of a mountain belt revealed by the trace element rhenium. *Earth and Planetary Science Letters* 403:27-36.

[2] Soulet G, Hilton RG, et al. (2018) Technical note: In situ measurement of flux and isotopic composition of CO_2 released during oxidative weathering of sedimentary rocks. *Biogeosciences* 15(13):4087–4102.

[3] Hardie SML, Garnett MHH, et al. (2005) Carbon dioxide capture using a zeolite molecular sieve sampling system for isotopic studies (^{13}C and ^{14}C) of respiration. *Radiocarbon* 47(3):441–451.

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To learn more about the ROC-CO2 project, visit https://roc-co2.weebly.com

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