Europlanet TA Scientific Report

PROJECT LEADER

Project number: 20-EPN-014
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Home Institution: GFZ Potsdam
TA Facility visited: CRPG Nancy

Project Title: **Constraining CO_2 uptake and release through chemical weathering pathways in a young, active orogen**

Scientific Report Summary.
(plain text, no figures, maximum 250 words, to be included in database and published)

Young, active orogens often retain an intact sedimentary cover that is composed of marine sequences, which can host large volumes of carbonate and sulfuric acid-producing minerals, such as pyrite. Unlike silicate weathering, which is responsible for CO_2 drawdown over geologic timescales, sulfuric acid weathering of carbonates has the potential to release CO_2 into the atmosphere that was previously trapped in rock. The goals of this study are to calculate the overall carbon budget for the Central Apennines, a young, active orogen, and to understand the mechanisms for the release and drawdown of CO_2 in this landscape. Compiling a representative assessment of chemical weathering fluxes requires an understanding of the possible variability between seasons. To this end, the objective of my TA visit to the CRPG in Nancy, France was to process riverine water samples collected in winter of 2021 for $\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$, and $\delta^{13}C_{DIC}$. These samples are replicate analyses of samples from summer 2020, and provide a direct comparison of isotopic signatures between the hot and dry summer versus the wet and cool winter. Preliminary results show that $\delta^{34}S$ signatures are similar between winter and summer for spring and groundwater samples, whereas river samples are more enriched in summer. Further analysis and results from other isotopic systems will help elucidate the major sources of variability that we observe in the river samples.

The purpose of the TA visit was to process river water samples collected from 55 locations in the Central Apennine Mountains of Italy during winter 2021. With the exception of 5 samples collected from new locations, the remaining 50 are replicates of samples collected from the same locations during the summer of 2020. Previous work (Erlanger, 2020) has found that major ion concentrations in the Northern Apennine Mountains can vary by a factor of 2 between winter and summer. Thus, one of the first-order goals of this project has been to constrain the overall variability in major dissolved ions and isotopic signatures of river water between the hot, dry summer and the cool, wet winter. The project funded by the Europlanet 2024 transnational visit is part of a larger postdoctoral research project funded by the Swiss National Science Foundation, titled "Carbon sink or carbon emitter? Determining the carbon budget of a young orogen and constraining the impact of anthropogenic sulfuric acid on the carbon cycle", of which I am the principal investigator. The goal of this postdoc project is to quantify the carbon budget of the Central Apennine Mountains, in order to understand whether this orogen is a net carbon sink or carbon emitter. Additionally, previous work in the Northern Apennines has revealed both natural and anthropogenic sources of riverine sulfate. The Central Apennines has a number of large sedimentary basins formed due to normal faulting (e.g. Fucino Basin), which are often used for agriculture, so another objective of this study is to isolate potential anthropogenic sources of sulfate to the river water.

Active orogens are classically recognized as the dominant source of weathering fluxes, as they provide the majority of fresh minerals to the surface by uplift and erosion. In mature orogens, silicate rocks dominate the surface geology, whereas young orogens are commonly characterized by marine sedimentary sequences that can host significant volumes of carbonate and sulfuric acid-producing sulfides (such as pyrite). Therefore, this developmental stage of orogenesis is expected to be most strongly influenced by sulfuric acid weathering, with important implications for the carbon cycle. As a young, active orogen that exposes an intact sedimentary cover dominated by Mesozoic carbonates, the Central Apennines are an ideal setting to address this knowledge gap.

Quantifying the carbon budget of an orogen require constraints on the CO_2 release or uptake resulting from the weathering effect of carbonic acid and sulfuric acid on silicates and carbonate. The first step in assessing the weathering effect of these acid is to deconvolve the natural and anthropogenic sources of sulfate and carbon in the landscape, by measuring $\delta^{34}S(SO_4)$ and $\delta^{18}O(SO_4)$, as well as $DI^{13}C$. The CRPG in Nancy is one of the few institutions in Europe equipped to measure $\delta^{34}S(SO_4)$ and $\delta^{18}O(SO_4)$, as well as $DI^{13}C$, which my institute is unable to measure in-house.

I processed my summer river samples at the CRPG in October of 2020 and organized a second visit for in June, 2021, under the Europlanet 2024 transnational access (TA) visit. The trip to the CRPG was planned for a duration of 6 working days, based on the Europlanet proposal timeline.

Train travel from Berlin to Nancy was booked for 13.07.2021, with a return trip planned for 26.06.21. Work related to the TA visit was performed from 14.07.21-21.07.21, excluding the weekend. The return trip from Nancy to Berlin was planned for 26.07.21 (arrival in Berlin at 00:15 on 27.06.21), since I took time for a personal visit in France once my official TA visit to the CRPG was completed.

Due to the different sample preparation times required for $\delta^{34}S(SO_4)$, $\delta^{18}O(SO_4)$, and $DI^{13}C$, sample preparation and measurement were performed concurrently, in order to be efficient with my time during the TA visit. Preparing the ^{34}S samples required performing column chemistry, to extract the anions from the water samples (Figure 1). These samples were then dried down and acidified prior to running them through the Neptune MC-ICPMS. Acquisition of MC-ICPMS data required, as planned, three days of instrument time. To prep the $\delta^{18}O$ samples, the water samples were evaporated down to a volume of 50 mL, and a BaCl solution was added to the water, in order to precipitate $BaSO_4$, from which the $\delta^{18}O$ is measured on a Thermofisher EAIsolink-Delta V IRMS. To prepare the sample for $DI^{13}C$ measurements, the samples and H_3PO4 were added to glass vials. The samples were then vaporized in the vials and the isotopic composition of the dissolved inorganic carbon within the remaining CO_2 gas was measured with a Thermofisher EAIsolink-Delta V IRMS. $DI^{13}C$ and $\delta^{18}O$ analyses required a total of 5 days of instrument time and finished running after the TA visit itself. Analytical assistance was provided by Guillaume Paris and Thomas Rigaudier from the CRPG. They took care of the data processing that occurred after the TA visit itself. They also prepared everything that was required before the TA visit to ensure smooth running of the samples (cleaning necessary vials and chemistry material, preparing the columns and reagents for chemical extractions, and purchasing material for the instruments).

Figure 1. Anion column chemistry setup for a batch of water samples being prepared for $\delta^{34}S$ measurement.

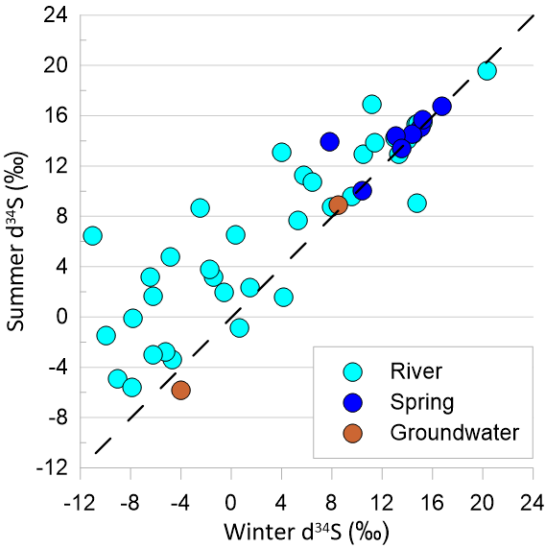


Figure 2. Comparison of winter versus summer $\delta^{34}S$ values of water from the Central Apennines.

New results for $d^{34}S$ (Figure 2) illustrate different trends between the winter and summer samples that reflect the source of the water. Samples collected from springs or from proximal river samples illustrate the same or similar $\delta^{34}S$ signatures between winter and summer, and lie along the 1:1 line. In contrast, the majority of river samples illustrate more enriched $\delta^{34}S$ signatures during the summer season, although a few river samples have slightly more depleted summer $\delta^{34}S$ signatures. These results are consistent with the variability in $DI^{13}C$ that we observe amongst the summer samples, which suggest that the spring samples are fed by deeper, thermal waters that interact with Triassic gypsum deposits at depth, producing enriched $\delta^{34}S$ values. The signature of the thermal water is dominated by the Triassic gypsum and thus, this signal may overprint any seasonal variability, or seasonal variability may be absent altogether. For the riverine samples, isotopic signatures of $d^{13}C$ and $\delta^{18}O(SO_4)$ will help to elucidate the source of the seasonal variability that we observe.

- Give details of any publications arising/planned (include conference abstracts etc)

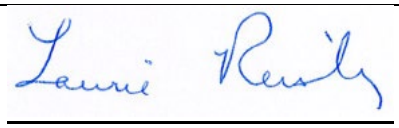
Planned publications using this dataset are to: 1) to deconvolve the impact of natural and anthropogenic sources of sulfate to the river and 2) To quantify the carbon budget of the Central Apennines. A third publication related to the larger postdoc project is also planned, using isotopic measurements of $d^{18}O(H_2O)$ and $d^{2}H$ that were performed at the GFZ in-house, and were thus not included in the Europlanet proposal and funding. Results will also be presented in international conferences such as EGU or Goldschmidt.

- Host confirmation

Please can hosts fill in/check this table confirming the breakdown of time for this TA project:

Dates for travel to accommodation for TA visit (if physical visit by applicant)	Start Date of TA project at facility	Number of lab/field days spent on TA Visit pre-analytical preparation	Number of days in lab/field site for TA Visit	Number of days spent in lab for TA Visit data analysis	End Date of TA project at facility	Dates for travel home (if physical visit by applicant)
Departed: 13-06-21 Arrived: 13-06-21	14-06-21	[0-3] 3	6	[0-2] 2 (post-visit)	21-06-21	Departed: 26-06-21 Arrived: 27-06-21

The host is required to approve the report agreeing it is an accurate account of the research performed.

Host Name	
Host Signature	
Date	

- Project Leader confirmation

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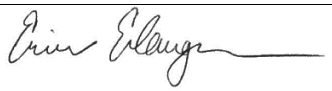
Project Leader Name	**Erica Erlanger**

Project Leader Signature	
Date	**01.07.2021**