Evaluating the contribution of Marine Aerosols to the Mo Surface Water Cycle

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1. Project description

The project aims to deliver a robust evaluation of the isotope budgets of different molybdenum (Mo) sources in continental environments. This is important not only to studies of the modern Mo surface cycle (e.g. for discrimination between natural and anthropogenic airborne Mo), but also as a key input parameter in models reconstructing paleo-oceanic environmental conditions. All models of the ancient global Mo cycle throughout the geological record (Mo as paleo redox proxy) depend on constraints from modern Mo fluxes. Mo isotopic composition (δ^{98}Mo) of river waters around the globe are significantly enriched in heavier Mo isotopes relative to their Mo source (bedrock). A hitherto unconstrained potential source of elevated δ^{98}Mo is precipitation of marine aerosols (ocean water: elevated δ^{98}Mo) as indicated by Sr isotope ($^{87}Sr/^{86}Sr$) and δ^{98}Mo signature data from small streams in the vogues mountains, France (Nägler et al. 2020). This additional 'heavy Mo source' would be a new component in the mass balance and - in contrast to the canonical hypothesis of light δ^{98}Mo retention in soils - not been erased by steady state conditions. Based on the scarce literature and own Mo concentration data a singular quantity of 20 L of precipitation is needed to obtain the amount of Mo necessary for δ^{98}Mo measurements (≥ 20 ng).

Given these analytical constraints, we face the difficulty to obtain 20 L of precipitation without contamination by a few nanograms of Mo from sampling equipment. To resolve this problem, we chose the approach of snow sampling. The Mo isotope-, Sr isotope-, trace element and δ^{18}O compositions of snow samples from three locations with varying proximity to the nearest coastline and at different altitudes are targeted:

1) High Altitude Research Station Jungfraujoch (HFSJ); chosen because aerosols as well as atmospheric δ^{18}O have been studied here for a long time; anthropogenic aerosol contribution is low; snow is readily available; the altitude is significantly different from the other sampling sites; Aerosols can originate from the both sides of the alps, and the origin of snow can be readily traced by its δ^{18}O signature. Interpretation of the Jungfraujoch (JFJ) results will strongly rely on the continuous records from the JFJ station (mainly δ^{18}O and meteorological conditions). 4 sampling campaigns at the HFSJ will be necessary to investigate seasonal variations.

2) Strengbach Catchment, Vogues Mountains, France, http://ohge.unistra.fr, monitored "field laboratory" since > 30 years; here Nägler et al. (2020) found evidence for a Mo contribution from marine aerosols in the surface waters; making the site a prime source for the current project.

3) East coast of Newfoundland & Labrador, Canada: Existing collaborations, abundant snowfall as well as verified contribution from seaspray to precipitation were the base of this choice. This site is the extreme counterpart to the HFSJ.

Unfortunately, the current Covid-19 situation forces us to choose alternative sites for 2 and 3 this winter: The Swiss Jurassic Mountains (Chasseral) to be the intermediate sample between the Atlantic ocean and HFSJ, and potentially the west coast of Ireland to replace 3 as near-coastal samples, this time rainwater.

Distinguishing between marine aerosols, continental and/or organic dust and anthropogenic particulates is essential to this study and will be carried out via the parallel trace element analysis of dust extracted from snow samples.

An additional dataset of stream waters draining the snow sampling areas of the Jungfraujoch also complements the primary precipitation data to help identify the controlling mechanics altering the initial δ^{98}Mo of the snowmelt as it enters the surface cycle. The stream waters included are as followed:

1) Trümmelbach catchment: meltwater draining the Eiger Glacier to the west of the sampling locations of the HFSJ, interacting with Jurassic carbonate rocks with likely differing δ^{98}Mo signatures.

2) Anunbach catchment draining the Jegi Glacier and/or streamwaters draining the Anunglacier: depending on conditions underfoot, these glaciers are the closest readily-accessible glacier/ snowmelt-draining stream waters to the Jungfraujoch on the southeast side of the sampling region of the HFSJ.

2. Progress 2020: Field work (i.e. activities outside perimeter of the Research Station and Sphinx):

Snow samples were collected during two sampling excursions in July and November 2020. During the summer excursion we collected the first two samples (7/20JFJ-01 and -02;) and tested the equipment (Figure 1 and 2). Prior to the first sampling campaign all material necessary for snow collection (e.g. barrels, shovels, tapes etc.) has been exhaustively tested in the lab for potential contamination with Mo and Sr.

Figure 1. Sampling 2. November 2020, Jungfraujoch. Details in Figure 2.

Figure 2. 'Mo free' Sampling: All plastic (PE) material, no metal parts; left shovel, 60 L barrels with double plastic bags as liners; right: The protruding part of the plastic bags is rolled in and secured with tape.

Based on the experiences of the first excursion at the HFSJ, during the second sampling excursion 8 samples were collected (11/20JFJ-03 to -10). This time samples were collected after a period of snowfall from two levels within the snow column. The two sampling periods will serve as a comparison between summer and winter snow accumulations.

Figure 3. Test setup of rainfall-collection equipment.

Three stream water samples were collected from the Trümmelbach catchment in August 2020, sampling directly below the Eiger Glacier where the water flows over bare carbonate rock, at a middle section of the catchment where soil and vegetation increases in volume, and on the valley floor just before the confluence with the Weisse Lütschine. Additionally, a test sample of rainwater in Dublin, Ireland was collected in December 2020 to test the method of collection using only the pre-cleaned material used for snow collection i.e., PE plastic bags and PTFE containers only (Figure 3), to minimise addition of unwanted Mo from equipment and handling. The first sampling of snow at the Chasseral Region is scheduled for the 21.01.2021.

3. Results

For snow samples from the first campaign in late summer 2020 chemical and water isotope ($\delta^{18}O$, $\delta^{2}H$) of snow samples have been produced. These data are supported by similar data produced on the three creek waters that form the discharge of melt-water from the Eiger- and Guggi-glaciers in the valley south of Kleine Scheidegg (East of Biglenalp). The data confirm the enrichment of chemical compounds and heavy water isotopes by cycled melting-freezing-evaporation effects during the summer months. Comparison with data collected in early winter (sampling performed), spring and early summer will be of high interest also with respect to the expected different accumulation of Mo during the seasons.

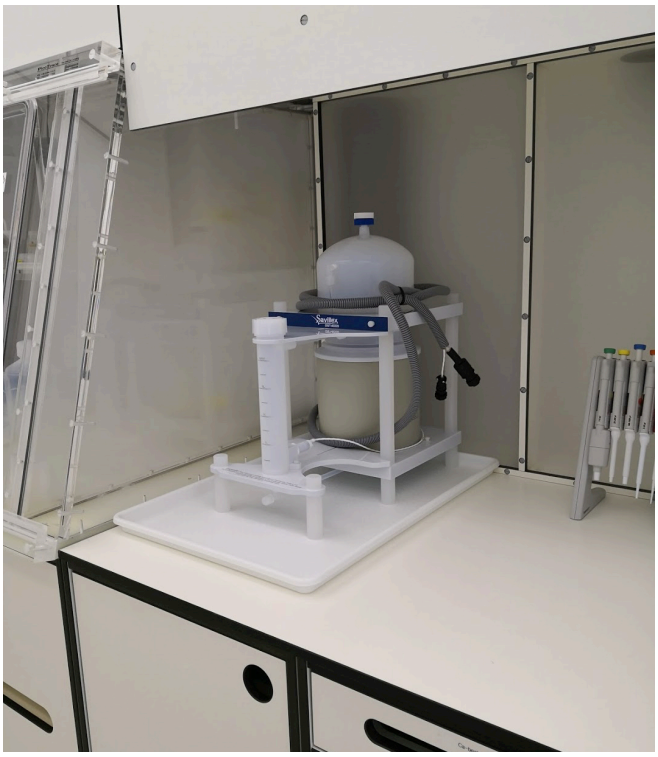

Figure 4. Distillation unit for evaporating snow samples.

Preliminary Mo data of snow samples point to a concentration of 0.07 nM Mo. This is about 20 times less than the Mo concentration in the measured streams, but ca. 7 times the Mo concentration of the only rainwater sample from the Strengbach catchment, vogues mountains, France presented in Nägler et al. (2020). The source of the Mo will be approached by δ^{98}Mo and trace element data. Recently the first samples passed the evaporation process (Figure 4).

A first successful δ^{98}Mo measurement demonstrates the principal feasibility of the method. Its result is in line with a natural, continental source. Thus - as expected - the samples from the Jungfraujoch appear to be suitable as a representative of the continental Mo end member contribution for mixing models of European precipitation sources in terms of Mo concentration and isotope composition.

References

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