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, and in particular the potential contribution of sea spray to Mo isotopic composition (δ^{98}Mo) of river waters, as outlined in our contribution to the Activity Report 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. Measurements of Mo isotopes in precipitation are currently at the limit of analytical possibilities due to the very low Mo contents. Based on the scarce literature and own Mo concentration data a quantity of 10-20 kg of precipitation is needed to obtain the amount of Mo (≥ 20 ng) necessary for δ^{98}Mo isotope measurements. As it is extremely difficult to obtain 20 L of rain without contamination by a few nanograms of Mo from sampling equipment, we have chosen the approach of snow sampling. Distinguishing between marine aerosols, continental and/or organic dust and anthropogenic particulates is essential to this study and is being carried out via the parallel δ^{98}Mo, ^{87}Sr/^{86}Sr and trace element analysis of atmospheric dust extracted from snow samples.

Snow samples from three locations with varying proximity to the nearest coastline and at different altitudes were targeted:

1. HFSJG; 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, and so is the difference in distance to a coast. Snow samples were collected during three sampling excursions in July and November 2020, and in October 2021, targeting fresh winter snow after a snowfall event in November and targeting compacted summer snow in July and October. The majority of data obtained are from this location.
2. Strengbach Catchment, Vogues Mountains, France (http://ohge.unistra.fr, monitored field laboratory); here, Nägler et al. (2020) found evidence for a Mo contribution from marine aerosols in the stream waters; making the site a prime source for the current project. Unfortunately, snowfall events in the Vogues Mountains are restricted to deep winter and thus correlated with increasing Covid-19 indices in 2020-2021, limiting the possibilities for sample collection. Alternatively, in early 2021, we chose a sampling site in the Swiss Jurassic Mountains (Chasseral), as a location intermediate between the Atlantic Ocean and HFSJG. Only in November 2021 it was finally possible to collect samples from the Vosges Mountains with our own equipment.
3. East coast of Newfoundland & Labrador, Canada: Existing collaborations, abundant snowfall as well as verified contribution from sea spray to precipitation were the base of this choice. Unfortunately, this site (as well as the planned alternative, Norway, December 2020) could not be sampled due to Covid-19 travel and laboratory access restrictions for our collaborator in St. John's, Newfoundland.

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 Jungfrau region snow cap beneath the Eiger Glacier to the west of the sampling locations of the HFSJG, representing the first interaction between precipitation and Jurassic carbonate bedrock with likely differing δ^{98}Mo and ^{87}Sr/^{86}Sr signatures. Little to no soil formation or weathering surfaces exist here due to the high intensity physical weathering environment and steep slopes. The particulate fraction of the stream waters has also been collected and will be analysed to provide an estimate of the δ^{98}Mo signature of the bedrock as well as localised dust from this area.

1. Anenbach Catchment: meltwater draining the Jungfrau region snow cap beneath the Jegi Glacier to the south of the sampling locations of the HFSJG. Snowmelt flows here over the bare rock face composed mainly of granitoids and schists, providing contrast to the carbonates of the west. Particulates were also collected and analysed.

2. **Progress 2021**

A total number of 13 samples were collected in the three campaigns at HFSJG (2 samples in July 2020, 8 samples in November 2020 and three samples in October 2021). One sample was collected from the Vosges mountains in January 2021 and a further 3 samples were collected in November 2021. Two samples were collected from the Swiss Jura Mountains in January 2021. Three stream water were collected from the Trümmelbach catchment in August 2020 and 3 from the Anenbach catchment in September 2021

Table 1. Current progress and planned analysis of snow and stream water, where X indicates completed analysis.

Date	Sample ID	Mo iso-topes	Sr iso-topes	H+O iso-topes	Major ions	Trace elements	Dust/part-iculates
Jungfraujoch							
21.07.2020	7/20-JFJ01	X	X	X	X	Spring 22	X
21.07.2020	7/20-JFJ02	N/A	N/A	X	X	Spring 22	Jan.22
02.11.2020	11/20-JFJ03	X	X	In progress	In progress	Spring 22	Jan.22
02.11.2020	11/20-JFJ04	X	X	In progress	In progress	Spring 22	Jan.22
02.11.2020	11/20-JFJ05	X	X	X	X	Spring 22	Jan.22
02.11.2020	11/20-JFJ06	X	X	X	X	Spring 22	Jan.22
02.11.2020	11/20-JFJ07	X	X	In progress	In progress	Spring 22	Jan.22
02.11.2020	11/20-JFJ08	X	X	In progress	Spring 22	Spring 22	Jan.22
02.11.2020	11/20-JFJ09	X	X	In progress	Spring 22	Spring 22	Jan.22
02.11.2020	11/20-JFJ10	X	X	In progress	Spring 22	Spring 22	Jan.22
12.10.2021	10/21-JFJ11	Jan.22	Jan.22	In progress	Spring 22	Spring 22	
12.10.2021	10/21-JFJ12	Jan.22	Jan.22	In progress	Spring 22	Spring 22	
12.10.2021	10/21-JFJ13	Jan.22	Jan.22	In progress	Spring 22	Spring 22	
Chasseral							
21.01.2021	01/21-CHL01	X	X	In progress	Spring 22	Spring 22	Jan.22
21.01.2021	01/21-CHL02	X	X	X	X	Spring 22	Jan.22
Strengbach							
--.01.2021	01/21-STR01	X	X	X	X	Spring 22	
11.11.2021	11/21-STR02	Jan.22	Jan.22	Spring 22	Spring 22	Spring 22	
11.11.2021	11/21-STR03	Jan.22	Jan.22	Spring 22	Spring 22	Spring 22	
11.11.2021	11/21-STR04	Jan.22	Jan.22	Spring 22	Spring 22	Spring 22	
Trümmelbach							
15.08.2020	08/20-TRB01	X	X	X	X	Spring 22	
15.08.2020	08/20-TRB02	X	X	X	X	Spring 22	
15.08.2020	08/20-TRB03	X	X	X	X	Spring 22	
Anenbach							
27.09.2021	09/21-ANB01	X	X	In progress	In progress	Spring 22	
27.09.2021	09/21-ANB02	X	X	In progress	In progress	Spring 22	
27.09.2021	09/21-ANB03	X	X	In progress	In progress	Spring 22	

2. Results

Four snow samples from the HFSJG, one sample from the Vosges and one sample from the Jura Mountains have been analysed for stable water isotopes ($\delta^{18}O$, $\delta^{2}H$) as well as major ions. The $\delta^{18}O$ and $\delta^{2}H$ data fall on the global meteoric water line (GMWL), with isotopically lighter water evident in the winter samples. This confirms the enrichment of chemical compounds and heavy water isotopes by cycled melting-freezing-evaporation effects during the summer months. Three stream water samples from the Trümmelbach stream waters that form the discharge of melt-water from the Eiger- and Guggi-glaciers, also collected in the summer, fall close to the summer snow samples or in between, reflecting the seasonal changes in snow precipitation and snow melt water.

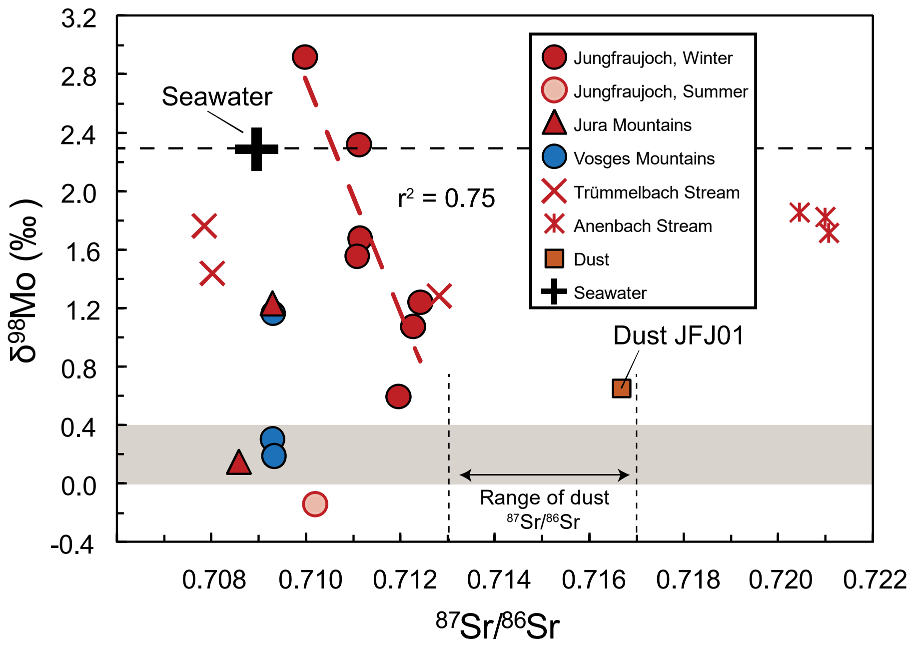

Figure 1. δ^{98}Mo vs. $^{87}Sr/^{86}Sr$ for all samples analysed so far as well as one dust sample extracted from sample 7/20-JFJ01. Dashed red trend line and r^2 value refers only to winter HFSJG samples. Black plus sign indicates modern seawater composition. Vertical dashed lines indicate range of $^{87}Sr/^{86}Sr$ for 3 analysed dust samples. Horizontal dashed line indicates seawater δ^{98}Mo, and horizontal grey bar indicates range of typical continental δ^{98}Mo values.

Snow samples average a Mo concentration of 0.04 nM. HSFJG samples alone range from 0.004 to 0.032 nM. Samples from the Jura Mountains are in a similar range of 0.01 to 0.02 nM. This is about 2 orders of magnitude less than the Mo concentration in the measured streams, but is similar to the Mo concentration of the only rainwater sample from the Strengbach catchment, Vosges mountains presented in Nägler et al. (2020) of 0.01 nM. The first sample collected in January 2021 from the Vosges Mountains and analysed here is an order of magnitude higher than this, at around 0.1 nM. The reason for this is not yet clear. δ^{98}Mo from the snow sample set analysed so far range from -0.14 to 2.9 ‰ with an average of 1.10 ‰ (n = 12, Figure 1). Due to the very low Mo contents of the samples, most data has been corrected for background blank within a reasonable limit. Thus, data are mostly above (almost) all continental sources and indicates that precipitation provides a small, but potentially significant contribution to river water compositions even in remote areas. Stream water samples from the Trümmelbach catchment and the Anenbach catchment, which represent immediate drainage waters from the Jungfrau region snow field, are also isotopically heavy between 1.28 and 1.86 ‰, and are largely coherent despite the differing bedrock with which the snow melt comes into contact. It is not yet constrained whether this reflects drainage of a primarily isotopically heavy snow pack.

Although there is so far no obvious trend associated with distance from the sea nor altitude, an interesting trend that is currently emerging as more data is becoming available is the correlation between δ^{98}Mo and [Mo] in the HFSJG samples, where lower [Mo] is associated with heavier δ^{98}Mo and vice versa. This trend is also evident, and is perhaps elucidated by, analysis of the Sr isotopes (Figure 1). A negative correlation is also seen in the winter samples from the HFSFG, where a lower (less radiogenic) $^{87}Sr/^{86}Sr$ is associated with heavier δ^{98}Mo compositions, and higher (more radiogenic) $^{87}Sr/^{86}Sr$ is associated with lighter δ^{98}Mo compositions. It appears that a mixing relationship is present between two reservoirs, one approaching the isotope composition of continental material, and the other approaching that of seawater (Figure 1). If true, further geochemical analysis of major ions and trace elements along with a numerical modelling approach will be able to distinguish whether a marine signature is indeed evident in the inner-continental, high altitude environment at the HFSJG.

Final samples from the Vosges and HFSJG passed the evaporation process and will be analysed for δ^{98}Mo and Sr isotopes in January 2022 (Table 1). The identification of the end member Mo sources will have to await the final analysis of the complete set of major, minor and trace element data.

References

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Collaborating partners

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Scientific publications and public outreach 2021

Conference Papers

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