Molybdenum speciation and distribution in ancient euxinic shales by μXRF and μXANES spectroscopy

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Molybdenum is a redox sensitive metal used to investigate oxygen content in ancient oceans from sedimentary records. Specifically, Mo enrichment, Mo/TOC ratio and ^{98}Mo-isotopic signature in black shales are determined to characterize euxinic deposition, seawater Mo concentration, and global ocean oxygenation, respectively. However, these approaches are based on bulk rock analyses without a comprehensive understanding of chemical burial pathway(s). Here, we bridge this gap using μ-XRF and μ-XANES to investigate Mo speciation and distribution in drill core samples from the ~500 Ma Alum shale formation.

The Mo distribution in our shale samples demonstrates a homogenous enrichment (~100 ppm) relative to average upper crust (~ 1 ppm), superimposed by enrichments in 0.1 mm thick lenses within certain sedimentary lamina. The μ-XRF elemental maps show a consistent correlation of Mo and Fe abundance and that Mo-rich lenses are particularly poor in Rb (e.g. clay minerals) and Br (e.g. organic matter). However, the apparent decoupling between Mo and organic matter in the lenses is tentative and needs further validation. The Mo speciation was determined using μXANES spectra and compared to bulk XANES analyses of modern euxinic sediments where two types of Mo compounds were identified: Mo(IV)-S and Mo(VI)-O [1]. In our samples the Mo-rich lenses host both species, while the matrix contains only the Mo(IV)-S compound.

The Mo-Fe association is consistent with our previous study showing that both Mo species display an Fe atom in the second or third shell. Further, the reduced Mo(IV)-S compounds appear to be pristine precipitates from Cambrian seawater, whereas post-depositional oxidation cannot be ruled out for the oxidized Mo(VI)-O species. Conclusively, the pristine Mo(IV)-S in the matrix may serve as better targets for paleoredox investigations relative to bulk rock analysis.

[1] Dahl *et al.* (2013) *GCA* **103** *213-231,* [2] Helz *et al.* (1996) *GCA* **60** *3631-3662*

Trace-gas measurements in firn and ice cores using CRDS instruments

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Ice cores and polar firn air provide a unique means to reconstruct polar temperature as well as atmospheric composition changes. They notably help to understand the feedbacks at work between natural climate variability and biogeochemical cycles controlling the atmospheric composition.

The iconic curves of greenhouse gas (CO_2, CH_4, N_2O) concentration changes over the last 800,000 years have been produced through painstaking discrete measurements over years of laboratory work. Stable isotopic ratios of the three greenhouse gases (used to better understand the causes of greenhouse gas concentration changes) are also investigated through discrete measurements. They typically require a full day work in the laboratory for acquiring one or two data points, and they are still far from reaching the time span and resolution of mixing ratio measurements.

Since four years, the availability of Cavity Ring-Down Spectroscopy (CRDS) instruments with enough sensitivity and precision for ice core applications, has largely changed the way firn air and ice core samples are handled. I will show and discuss the results recently obtained on firn air measured in the field and on different ice cores, the latter combining a continuous-flow analysis (CFA) extraction technique and a CRDS instrument, using either WS-CRDS (Picarro) or OF-CEAS (SARA) technology. Clear advantages of these new analytical settings are : speed of measurements, instrumental precision, saving of raw material, compatibility with field work, resolution of fine features along the core. But as with any new technique, there are drawbacks. Notably the difficulty to obtain accurate measurements with the coupled CFA-CRDS setup (calibration with discrete measurements is still needed), and the smoothing and possible drift of the CFA system.

I will also provide a short review on our current developments at the interface between laser physics and ice core / paleoclimate applications. This concerns the OF-CEAS measurements of trace-gas isotopic ratios, as well as an embedded OF-CEAS spectrometer for real-time *in situ* measurements of water isotopes and greenhouse gases inside an ice sheet.

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