	Experiment title: **Bromine speciation as a paleoenvironmental proxy**	**Experiment number**: EV373
Beamline: BM16	**Date of experiment**: from: 27 August 2020 to: 14 September 2020	**Date of report**: 13 Feb 2021
Shifts: 15 allocated, 45 scheduled	**Local contact(s)**: PROUX Olivier, ROVEZZI Mauro	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Geraldine Sarret, ISTerre, UGA & CNRS, Grenoble*

Charline Giguet-Covex, EDYTEM, USMB & CNRS, Chambery *

Stéphane Guédron, ISTerre, UGA & CNRS, Grenoble*

Anne Lise Develle, EDYTEM, USMB & CNRS, Chambery

Clément Roy, ISTerre, UGA & CNRS, Grenoble

Context

In paleoenvironmental archives such as peat and lake sediments, bromine is generally correlated with organic matter. However, its status of proxy of biological productivity is debated. The purpose of this experiment was to study Br speciation for a collection of well characterized sediment cores from mires and lakes with contrasted typologies, as well as present terrestrial and aquatic plants, litter and soils for one of the lakes.

We used Br K-edge bulk HERFD-XANES spectroscopy on FAME UHD. The results will allow to assess the relationship between Br speciation and environmental conditions. In addition, the study of the whole series, from living plants to deep sediment, will allow us to describe the geochemical transformations of Br during plant decomposition, burial and sediment diagenesis. These data should clarify whether Br speciation can be used as a paleoenvironmental proxy.

Report

The experiment was performed in 7/8 mode, 200 mA. Because it was the first experiment at the restart, and some tests were necessary, more beamtime was kindly granted to us. We actually started the measurements on Sept 2nd and finished on Sept 15, 8h, with two machine days in-between, i.e., 12 days, 36 shifts.

Spectra were recorded at 15°K with a He cryostat to limit radiation damage. The monochromator was a Si(220) double crystal. The HERFD detection was done with 12 Si(880) crystals analyzers directed on a 2D imixpad detector. We tested another detector (Ktech), but the signal was worse. Energy calibration was done by recording every 10 spectra a Pt foil placed in position 2 in transmission (L_2 edge at 13.273 eV).

The acquisition mode was step by step. We had to do short scans (1s/pt, 7 min for the whole scan) and to change the beam position between each scan in order to avoid radiation damage. 10 standards were recorded, including bromophenol (aromatic Br), bromoeicosane (aliphatic Br), CTAB (inorg Br associated with an organic cation), inorganic Br (NaBr, KBr, LiBr, $PbBr_2$), two humic acids and one fulvic acid standards. We recorded the spectra for 42 sediment samples and for 2 aquatic plants. The detection limit was 10-20 mg kg^{-1} Br depending on the matrix. Some sediment layers, the terrestrial plants, and suspended particulate matter collected in the water column were below this limit, so we are missing some compartments with low Br content.

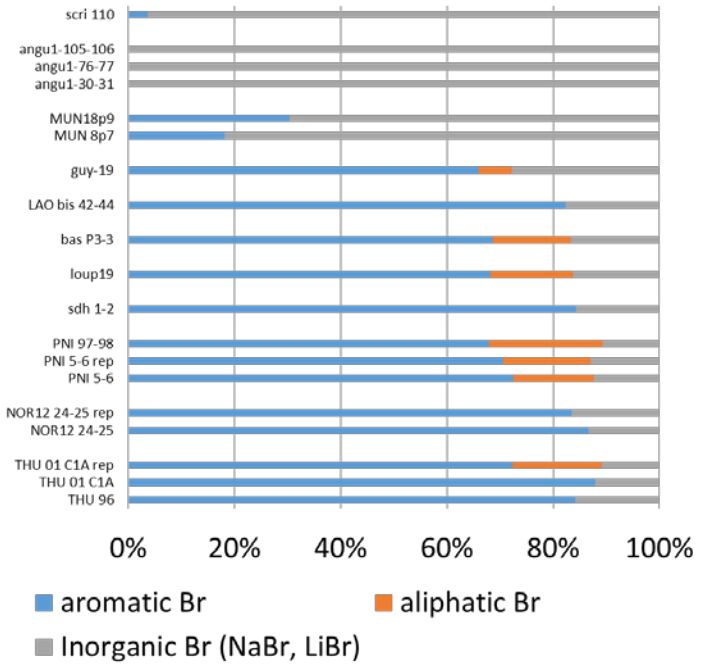

Figure 1: Br speciation obtained by LCFs of XANES spectra of a selection of sediment samples

Spectra were treated by principal component analysis, target transformation and then linear combination fitting (LCFs). Three components were sufficient to describe the system, including aliphatic Br, aromatic Br and inorganic Br. Contrasted Br speciation were obtained as a function of the environmental setting (Figure 1), but no change was observed as a function of sediment depth (one example shown in Figure 2). This contrasts with a previous study for marine sediments (Leri et al., 2010). A clear difference in Br speciation was observed between aquatic plants and the sediment (Figure 1), suggesting some change during plant degradation and incorporation to the sediment. Information on other sources is necessary to get a full picture of Br cycling in the system.

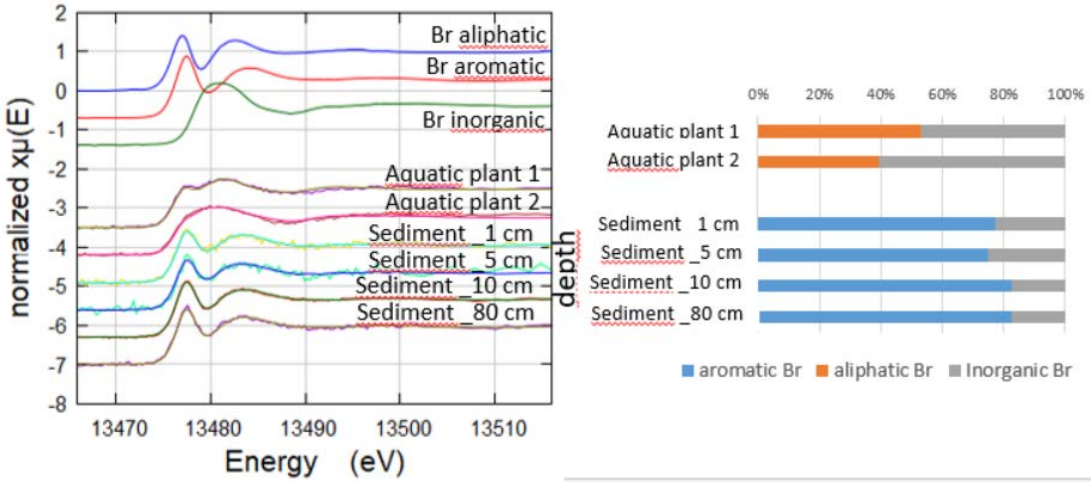

Figure 2: Example of plant and sediment spectra from the Laguna Pujzara mire/lake in Bolivia, and linear combination fits using three Br standards.

Conclusions: Original results were obtained on Br speciation in lake sediments, peatbogs and aquatic plants despite the fact that the samples with Br content < 10-20 mg kg^{-1} Br depending on the matrix. PCA including Br speciation determined by XANES, organic matter characteristics, carbon isotope ratio and total Br content, and other parameters is underway to understand which factors control Br speciation. Such understanding will allow us to refine our use of Br as a paleo environmental proxy. We hope we can complement our dataset of Br XANES spectra for samples at lower Br content in the future.

Reference

Leri, A.C., et al., Global Biogeoch. Cycles, 2010.