Standard Project

Experimental Report template

Proposal title: Refinement of Br speciation in silicate and carbonatic glasses : towards a better understanding of Br incorporation in geological melts.		**Proposal number:** 16-01 786
Beamline: BM16	**Date(s) of experiment:** from: 05/07/2017 to: 11/07/2017	**Date of report:** 10/02/2018
Shifts: 18	**Local contact(s):** Jean-Louis Hazemann	*Date of submission:* *12/02/2018*

Objective & expected results:

Br degassing at volcanic centres has been demonstrated to significantly affect the chemistry of the Earth's atmosphere, with the formation of BrO in cataclysmic volcanic plumes potentially triggering ozone destruction in the stratosphere. A better understanding (and consequent modelling) of Br solubility and degassing mechanisms requires understanding the compositional effect on Br speciation in geological melts. Up to now, Br speciation had only been investigated in peralkaline granitic compositions [1,2]. Furthermore, the results of EXAFS refinement from these studies is questionable (ie., quality of the fits with Artemis were not good enough and similar bond distances were for instance attributed to either Br-Na or Br-O bonds without further support) and the overall aim of this proposal was hence to obtain **refined HERFD-XAS** spectra on these haplogranite glasses, but also **natural intermediate compositions found in volcanic arcs (basalts, dacite and rhyodacite)** [3].

Results and conclusions of the study:

High-resolution HERFD-XAS spectra were collected on 2x2 mm (Hxh) polished chips of haplogranite, rhyodacite, dacite, andesite and basalt glasses containing from ~ 7 ppm ('degassed' compositions) to up to 3 wt% Br. The HERFD-XAS were acquired from 13400 to 13960 eV using the crystal analyser spectrometer at the newly commissioned FAME-UHD BM16 beamline. The experimental set-up also included a Vortex fluorescence detector placed at 90 ° from the incoming beam so as to compare HERFD and conventional XAS data. For all compositions, a minimum of 6 spectra (and up to 20) was acquired and merged with the Athena program to improve signal to noise ratio.

The experiments confirm the improved information obtained by HERFD versus conventional XAS. Both pre-edge and post-edge shapes suggest structural differences between the different compositions. Pre-edge features are found in haplogranite and rhyodacite glasses, *ie.,* the more polymerized compositions. While those were already noticeable in the conventional XAS, they are much better refined in the HERFD-XAS (Fig 1). Br K-edge pre-edge features have previously been attributed to 1s – (2,3)p transition in compounds where Br forms covalent bond (Br_2, HBr, brominated hydrocarbons) [4,5]. Furthermore there are obvious differences between the haplogranite (W001-Br2, which only contains Si, Al, Na and K) and the natural andesite, rhyodacite and basalts (which contain Si, Al, Na, K, but also 1-10wt% FeO_{tot} and 2-10 wt% CaO) (Fig. 2) [3]. As previous

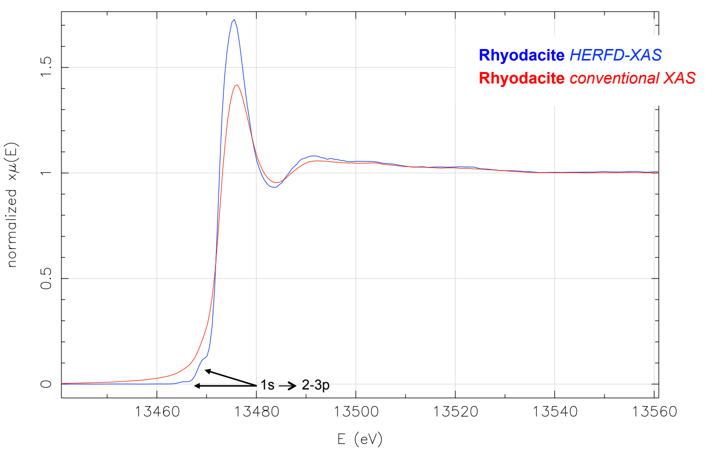

Fig. 1 : Comparison between the HERFD and conventional XAS spectrum of Br in rhyodacite glass. The arrows point to pre-edge features that were unresolved through conventionnal XAS.

XANES study on Cl-bearing (boro)silicate glasses suggested that in the presence of both Na and Ca, Cl preferentially form Ca-Clx species [4,6], we suggest Br could behave in the same way, ie., form Ca-Br_x species in the presence of Ca. EXAFS analysis is currently under way to test this hypothesis. A new proposal is also being submitted to the LUCIA beamline (SOLEIL) to conduct Na and Ca K-edge XANES analyses on the same samples and ensure the correct attribution of Br-Na or Br-Ca bond distances (in comparison to Br-O). The sum of these measurements should provide a more comprehensive view of Br structural environment in silicate glasses and melts, critical to a better understanding of Br degassing processing.

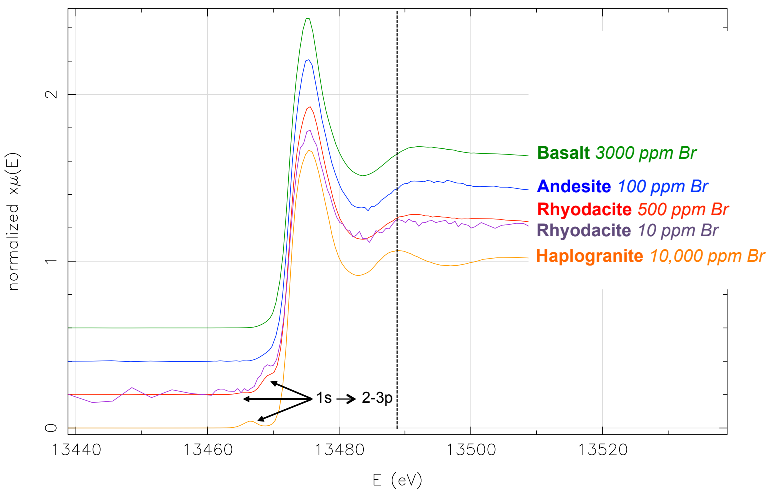

Fig.2 : HERFD spectra for the different glass composition.
The dotted line underlines major differences between Ca-free haplogranite and Ca-bearing natural glasses. The arrows show the pre-edge features in haplogranite and rhyodacite.
The spectrum of 'degassed' rhyodacite containing only 10 ppm of Br is represented on top of the same 'undegassed' composition.

Justification and comments about the use of beam time:
The comparison between HERFD- and conventional XAS spectra here collected confirms the future potential of this refined technic for the study of geological materials that are generally quite diluted (<100 ppm) [7]. While BM16 has only been opened to users for few months, the beamline was swiftly tuned for optimal measurements (< 2 shifts) and should hence enable analysis on a large number of samples in the future.

Publication(s):

[1] Cadoux et al., 2017. Chem. Geol. 452, 60-70. [2] Louvel, 2011. PhD thesis – ETH Zurich. [3] Cochain et al., 2015. Chem. Geol. 404, 18-26. [4] Evans et al., 2008. G^3 9, doi:10.1029/2008GC002157. [5] Burattini et al., 1991. J. Phys. Chem. 95, 7880-7886. [6] McKeown et al., 2011. J. Nuclear Mat. 408, 236-245. [6] Proux et al., 2017. J. Envir. Qual. 46, 1146-1157.