ESRF	**Constraints on sulfur isotopic fractionations at magmatic temperatures through isotopic and micro-XANES spectroscopic measurements of sulfur and iron in experimental and natural mafic glasses from arc magmas**	**EC-548**
Beamline: ID 21	**Date of experiment**: from: 30/09/09 to: 06/10/09	**Date of report**: 17/02/10
Shifts: **15**	**Local contact(s)**: Vincent De Andrade	*Received at ESRF:*

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These experiments aimed at providing the first data set on isotopic fractionation of sulfur vs its speciation with a direct application to natural samples from active volcanoes by studying experimental glasses and olivine-hosted melt inclusions and by combining SIMS measurements of $\delta^{34}S$ and XANES determinations of the sulfur speciation. The μXANES experiments were very successful since we got a series of spectra at the S *K*-edge on:

- Experimental sulfur-bearing andesitic glasses in equilibrium with crystallized pyrrhotite and anhydrite over the 830 to 1020°C temperature range, which show both sulfide and sulfate dissolved species as expected on the basis of the saturation of both pyrrhotite and anhydrite;

- The glass products of experimental isothermal decompression under reducing and oxidizing fO_2 conditions with 1 or 2 decompression steps. The starting samples consisted in crystal-free basaltic andesite glasses with known $\delta^{34}S$, initial H_2O and S concentrations;

- Olivine-hosted melt inclusions from mafic arc magmas from active volcanoes - Mt. St Augustine in Alaska; Krakatau and Galunggung in Indonesia - which were previously analyzed for major and volatile elements. Hence, at time of XANES experiments, the concentrations in S and Fe_{total} of each sample were available.

We obtained μXANES spectra at the Fe *K*-edge on the same series of experimental and natural samples. In addition, we measured 3 glasses totally reduced that demonstrate the excellent resolution of the Fe-XANES spectra (Fig. 1). XANES spectra were recorded in the transmission mode since all the samples were double-face polished with a thickness of on average 50-100 μm. We have repeatedly measured the Fe-foil in order to check the energy calibration. The unknown samples were measured with the same experimental conditions and together with a series basaltic glasses having Fe^{3+}/Fe_{tot} ratios varying from 0.10 to 0.48, as previously described (Bonnin-Mosbah, 2002; Métrich et al., 2006).

A total of 9 experimental glasses, 3 natural basaltic glasses and 21 melt inclusions have been measured for S and Fe, covering a large range of redox conditions. As an example, the µXANES spectra of water-S-rich basaltic melt inclusions trapped in olivine from Augustine volcano are typical of highly oxidized melts rich in sulfur dissolved as sulfate (Fig. 2a). For the first time, we have in association the µXANES spectra at the Fe *K*-edge (Fig. 2b).

The treatment of XANES spectra is in progress, as are the SIMS analyses for S isotopes.

The whole data set is almost complete. The first results will be presented at the Goldschmidt Conference next June (Mandeville et al., 2010).

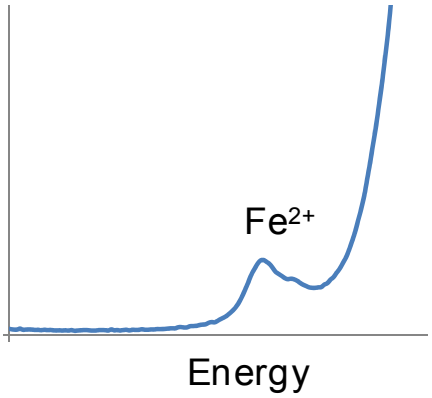

Fig. 1. µXANES spectrum at the Fe *K*-edge of a reduced basaltic glass with no Fe^{3+}. (ESRF – ID21)

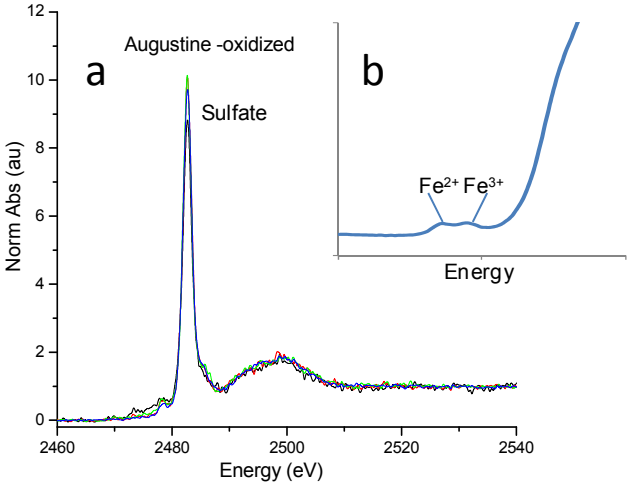

Fig. 2 µXANES spectra at the S (a) and Fe (b) *K*-edges in Augustine melt inclusions. (ESRF – ID21)

References:

Bonnin-Mosbah M., Métrich N., Susini J., Salomé M., Massare D., Menez B. (2002) Micro-X-ray Absorption Near Edge Structure at sulphur and iron K-edges in natural silicate glasses. *Spectrochim.. Acta, B*57, 711.

Métrich N., J. Susini, E. Foy, F. Farges, D. Massare, L. Sylla, S. Lequien & M. Bonnin-Mosbah (2006) Redox state of iron in peralkaline rhyolitic glass/melt. X-ray absorption micro-spectroscopy experiments at high temperature. *Chem. Geol* 231, 350-363.

Mandeville C., N. Shimizu, K. Kelley, N. Métrich (2010) Sulfur Isotope Variation in Arc Basalts Revealed By Secondary Ionization Mass Spectrometry. Measurements of Melt Inclusions. Goldschmidt Conf. Knoxville, Tennessee, USA, 13-18 June 2010.