



Experiment title: High temperature and in-situ micro-spectroscopy of iron in natural silicate melts and magmas

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The in-situ determination of the redox state of magmas and the relative variation of the $[\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})]$ atomic ratio during magma ascent from Earth mantle to the surface, is challenging because these silicate melts crystallized in response to the temperature decrease, the decompression and most of their volatile constituents (H_2O , CO_2 , SO_2 , HCl) are lost prior to eruption. Previous μXANES experiments performed on a series of basaltic glasses with $\text{Fe}^{3+}/\Sigma\text{Fe}$ atomic ratios varying from 0.05 to 0.84 indicated that (i) the energy resolution allows an accurate discrimination between the pre-edge features; (ii) the pre-edge features are observed at 7111.5 (Fe^{2+}) and 7113.2 eV (Fe^{3+}) and (iii) the area ratios between the Fe^{3+} and Fe^{2+} peaks vary linearly with the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio, for a restricted range of values (Total FeO being analyzed by volumetric titration and Fe_2O_3 by atomic absorption on the bulk samples) [1,2]. Using this correlation, we determined, for the first time, the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio in naturally quenched melt inclusions trapped in olivines and representative of the primitive magmas sustaining the current activity at Stromboli volcano in Italy [3].

The aim of these experiments (CH1363) was studying the chemical environment of iron in natural silicic rich glass/melt, in-situ within a range of temperature from 20 to 800°C, using XANES-EXAFS $\mu\text{spectroscopy}$ at the iron K-edge (7130 eV). These experiments were performed on glass inclusions trapped within natural hermetic containers as pure SiO_2 quartz crystals. The samples were placed in a water-cooled heater apparatus developed in our laboratory (Fig. 1). In addition, μXANES spectra were acquired on a series of Fe-Si rich glasses comparable in composition to the quartz hosted glass inclusions. New spectra were also done on some of the basaltic glasses previously studied.

The energy was scanned between 7050 and 7350 eV (some of them up to 7500 eV), using a fixed-exit Silicon (220) monochromator. The synchrotron X-ray source was demagnified down to a $2 \times 2 \mu\text{m}^2$ probe by using Fresnel zone plate lenses [4]. We worked in transmission mode.

A first result is that the correlation between the peak area ratio ($A_{Fe^{3+}}/A_{Fe^{2+}}$) and the $Fe^{3+}/\Sigma Fe$ ratios is obtained for both the basaltic and the silicic (rhyolitic) glasses, in a range of geologic interest ($Fe^{3+}/\Sigma Fe = 0.05-0.35$). Therefore, this correlation would be used for unknown glass samples with composition varying from basaltic ($\sim 50\text{wt}\% \text{SiO}_2$) to rhyolitic ($\sim 70-75 \text{wt}\% \text{SiO}_2$).

Different series of μXANES spectra were obtained on double-face polished glass inclusions at 20°C , and at different temperatures on glass/melt inclusions, by decreasing the temperature by step of 100°C between 800 and 20°C . Experiments have also been done at 20°C after experiments with different cooling rates. The figure 3 illustrates the pre-edge features in melt at 740°C and in glass at 20°C after experiments.

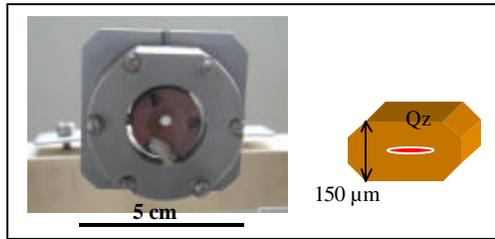


Fig. 1. The quartz crystals are double-face polished $\perp c$ and placed in the heater for in-situ μXANES experiments at the Fe K-edge.

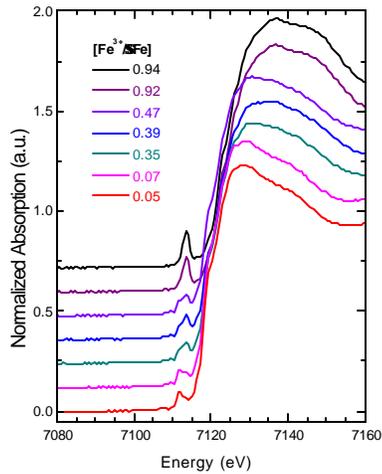


Fig. 2. μXANES spectra of Si-rich reference glasses with $Fe^{3+}/\Sigma Fe$ ratio varying from 0.05 to 0.94

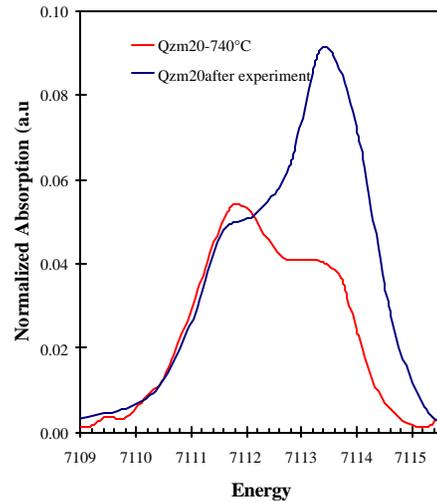


Fig. 3. μXANES spectra at the Fe K-edge of Si-rich melt and glass inclusion in quartz

References

- [1] Bonnin-Mosbah et al. (2001) *J. Non-Cryst. Solids*, 288, 103
- [2] Bonnin-Mosbah et al. (2002) *Spectr. Chim. Acta* **57**, 711
- [3] Métrich et al. (2002) *Geophys. Res. Lett.* **29/11**, 33-1.
- [4] Di Fabrizio et al., (1999) *Nature*, 401, 895