



Real-time probing of the XANES structures at the iron K-edge in natural water-rich peralkaline silicic glass/melt

N. Métrich (1), J. Susini (2), M. Munoz (3), S. Pascarelli (2) and D. Massare (1)

(1) Laboratoire Pierre Sue, CEA-CNRS, Saclay, France; (2) European Synchrotron Radiation Facility, Grenoble, France; (3) Laboratoire de Géodynamique des Chaînes Alpines, U.J.F., Grenoble, France; nicole.metrich@cea.fr / Fax: 33 1 69 08 69 23 / Phone: 33 1 69 08 85 11

The determination of the ferric-ferrous ratio in magmas is challenging because these silicate melts crystallize and lose most of their volatile constituents upon ascent. Recent X-ray microspectroscopy experiments at the Fe K-edge on peralkaline silicic glasses/melts, indicated that 1. the position of the pre-edge centroid of the $1s \rightarrow 3d$ transition correlates with the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios, 2. ${}^4\text{Fe}^{3+}$ prevails in highly oxidized glasses, using alkalis for charge balance and, 3. this ratio can be significantly overestimated in naturally cooled silicate glasses [1]. Recent work also shows that redox reactions can be monitored through XANES spectroscopy [2].

We provide, here, a series of *in situ* μ -XANES spectra collected at the iron K-edge (7112 eV) in the dispersive mode, on the XAS beamline ID24 at the ESRF. Acquisition times were particularly rapid so that real time monitoring of both redox state and speciation of iron in water-rich peralkaline rhyolite were performed. The experimental optics consisted in a pair of curved SiC mirrors in a Kirkpatrick Baez geometry followed by a Si(311) polychromator crystal and by an additional vertically focusing Si mirror [3]. The beam size on the sample was $15 \mu\text{m} \times 8 \mu\text{m}$ FWHM and the spectra were recorded using a CCD-based position sensitive detector, in the energy range 7100 – 7220 eV. Energy calibration was obtained by measuring spectra on a reference Fe foil sample.

The experiments were performed between 760 and 20 °C, in glass/melt inclusions trapped at high temperature (*i.e.*, 750°C) in quartz. The crystals were prepared as double face polished, 150 μm thick lamella. Different series of μ XANES spectra

were collected by decreasing the temperature with rates varying from 6.3 °C/sec to 10 °C/min. Preliminary results indicate that for a cooling rate of 10°C/min, changes in the ferrous and ferric pre-edge features occur at nearly 400°C; this temperature indicating most likely the glass transition. Other experiments are under reduction and suggest that the cooling rate plays a fundamental role in the oxidation state of iron in quenched samples. We will particularly focus on the effect of fast cooling rates on the oxidation/speciation of iron, and discuss the implications for predicting the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio in naturally cooled silicate glasses and glass inclusions.

[1] Métrich et al., *submitted to Chem. Geol.* (2004); [2] Magnien et al., *Chem. Geol.* 213, 253 (2004); [3] Pascarelli et al., *J. of Alloys and Compounds* 362, 33 (2004)