

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Effect of alkalis [Na/(Na+K) ratio] on the Fe oxidation state and local environment in phonolitic glasses.	Experiment number: ES-58
Beamline: BM08	Date of experiment: from: 17 July 2013 to: 22 July 2013	Date of report: 28 July 2014
Shifts: 15	Local contact(s): Dr. Angela Trapananti	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): *Cicconi M.R. *Giuli G. School of Science and Technology – Geology Division. University of Camerino (Italy)		

Report:

The preliminary data have been presented as oral contribution to the 5th Natural Silicate Glasses Conference (satellite workshop of the Goldschmidt Conference 2013).

The paper has been submitted as Regular Article to American Mineralogist.

Silicate glasses of phonolitic compositions have been synthesised to infer the effect of the [Na/(Na+K)] ratio on the Fe structural role and, as final goal, on the physical properties. Fe can exist in silicate melts in a variety of oxidation states and coordination geometries (e.g. Wilke et al. 2001; Giuli et al. 2002, 2011, 2012; Farges et al. 2004; Jackson et al. 2005; Rossano et al. 2008) and variations of the relative proportions of these species imply variations in <Fe-O> distances and bond strengths, thus affecting glass/melt polymerisation, Fe molar volumes, melt density and viscosity (e.g. Dingwell and Virgo 1987; Dingwell 1991; Liebske et al. 2003). Alkali content is one of the main parameters that affect Fe oxidation state in silicate melts (see Duffy 1993; Moretti and Ottonello 2003 and references therein), but no measurements are available up to now to quantitatively assess to which extent alkalis can modify Fe structural role in glasses/melts.

In this study, by using Fe K-edge XAS spectra (both XANES and EXAFS), we determined the Fe structural role (oxidation state, coordination number, bond distances) of phonolitic glasses to infer the influence of Temperature (1250 and 1400°C), [Na/(Na+K)] ratio (0.0, 0.25, 0.5, 0.75, 1.0, respectively) and redox environment (fO₂ from -0.68 to -11).

During this experiment we collected successfully XANES spectra for 40 different samples (synthetic glasses and Fe model compounds) with very good signal/noise ratio and EXAFS spectra for four samples (at least 3 spectra for each sample) at the Fe K-edge. Samples were prepared by smearing finely grounded powder on a Kapton tape and the spectra have been collected in fluorescence mode by using a high pure Ge-

detector. To check the energy reproducibility, a Fe foil was positioned in the REFLEXAS chamber in order to collect simultaneously the fluorescence for the samples and the transmission for the foil (internal calibration).

MAIN RESULTS, CONCLUSIONS and IMPLICATIONS

Quenched silicate melts, with variable $[\text{Na}/(\text{Na}+\text{K})]$ contents, synthesized in a wide range of redox conditions, have been successfully analyzed at the Fe K-edge by XAS, in order to assess the $[\text{Na}/(\text{Na}+\text{K})]$ effect on iron speciation.

The XAS spectra of the samples synthesized in air and at 1400°C show that the $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ ratio decreases by increasing the $[\text{Na}/(\text{Na}+\text{K})]$ ratio. This behaviour suggests that ferric iron is stabilised by cations with lower ionic potential and it prefers the tetrahedral coordination when sufficient alkalis are available for charge balance. The different $[\text{Na}/(\text{Na}+\text{K})]$ ratios strongly affect the $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ ratio for any oxygen fugacity conditions, as observed from the linear relationship between $\log(f\text{O}_2)$ and $\log[\text{Fe}^{2+}/\text{Fe}^{3+}]$.

Extended X-ray Absorption fine structure (EXAFS) data of the two end-member synthesized in air indicate that Fe^{3+} is in tetrahedral coordination with $\langle\text{Fe}-\text{O}\rangle = 1.88 \pm 0.02 \text{ \AA}$. This value is in agreement with previous studies on phonolitic and peralkaline rhyolitic glasses.

The experimental results show that at constant oxygen fugacity, the $[\text{Na}/(\text{Na}+\text{K})]$ ratio has a strong effect on the $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ ratio and that the substitution of K for Na stabilizes a higher amount of ferric iron.

The data here acquired demonstrate that models (i.e. Optical basicity; Duffy and Ingram 1976; Ottonello et al. 2001) are not able to fully reproduce the magnitude of the variations of the $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ ratio by changing relevant parameters, such as T and $[\text{Na}/(\text{Na}+\text{K})]$ ratio.